WADC TECHNICAL REPORT 54-371
SUPPLEMENT 1
ASTIA DOCUMENT No. AD 97301

INVESTIGATIONS OF RHENIUM

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SEPTEMBER 1956

AERONAUTICAL RESEARCH LABORATORY
CONTRACT AF 33(616)-232
PROJECT 7080
TASK 70659

WRIGHT AIR DEVELOPMENT CENTER
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UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
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FOREWORD

This report has been prepared by Battelle Memorial Institute under USAF Contract No. AF 33(616)-232 "Investigations of Rhenium". The present report is the final technical report on the project, and covers the second two-year period of work on this project, from June, 1954, to June 30, 1956. A previous WADC Technical Report, No. 54-371, describes investigations carried out during the period from June, 1952, to June, 1954. The contract was initiated under Project No. 7080, Task No. 70659, and administered under the direction of the Aeronautical Research Laboratory, Directorate of Research, Wright Air Development Center. Project engineers during the period covered by this report were Lt. John P. Hirth and Mr. James Poynter.

The Battelle work was divided among three research groups. Preparation of rhenium metal powder, and vapor pressure and electroplating studies were conducted by D. M. Rosenbaum, Principal Chemist, R. J. Runck, Assistant Division Chief, and I. E. Campbell, Chief, of the Inorganic Chemistry and Chemical Engineering Division. Physical, mechanical, and metallurgical properties determinations were studied by C. T. Sims, Assistant Division Chief, C. M. Craighead, Division Consultant (deceased), and R. I. Jaffee, Chief, Nonferrous Physical Metallurgy Division. W. W. Kleinschmidt, Laboratory Technician, D. N. Gideon and W. E. Nexsen, Principal Physicists, G. B. Gaines, Assistant Chief, and F. C. Todd and C. S. Peet, Chiefs of the Electronic Physics and Solid State Devices Divisions, respectively, conducted studies of physical and electronic properties.

Potassium perrhenate for chemical and metallurgical processing into rhenium metal was kindly donated by the Kennecott Copper Corporation through its subsidiary, The Chase Brass and Copper Company.

ABSTRACT

A new method is reported for the preparation of high-purity rhenium metal powder by reduction of a hydrolyzed rhenium halide. Fabrication and consolidation of this material is discussed. The effect of thoria additions on rhenium fabricability are evaluated, and additional information on the hot and cold working of pure rhenium given.

The electrical resistivity and specific heat of rhenium at room and elevated temperatures up to 2700 K are reported in detail. The electromotive forces generated by Re-Pt, Re-W, Re-Mo, and Re-Ta thermocouples were studied and the results are given.

Mechanical properties of several types of fabricated rhenium were measured and are discussed. These include tensile properties of annealed and cold-worked 10-mil strip, stress-rupture characteristics of 50-mil wire, work-hardening studies on rod, wire, sheet, and foil. The shear modulus of elasticity is reported and the temperature dependency of the modulus of elasticity up to 900 C given.

Electronic studies reported include results of the effect of additions of 2.0 per cent thorium as ThO_2 on the thermionic emission and an evaluation of the photoelectric work function of pure rhenium. The stability of rhenium and tungsten filaments in contact with alumina at 1600 C, and the stability of rhenium, tungsten, and molybdenum in carbonaceous atmospheres were evaluated and the results are discussed. Rhenium and tungsten filaments were studied for resistance to thermal and mechanical shock.

The resistance of rhenium to attack by molten metals was also evaluated and a discussion is included.

Arc-melted platinum-rhenium alloys containing up to 10 per cent rhenium were studied for fabricability and properties. A successful method for fabricating alloys containing up to 2.0 per cent rhenium was developed and is discussed, and the results of resistivity, thermal emf, tensile strength and ductility, hardness, and oxidation resistance determinations on these alloys are given.

The report also includes results of several investigations conducted outside Battelle at industrial or educational research establishments with rhenium supplied by this project.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Nathan L. Krisberg

NATHAN L. KRISBERG
Colonel, USAF
Chief, Aeronautical Research Laboratory
Directorate of Research

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INVESTIGATIONS OF RHENIUM

INTRODUCTION

This investigation of rhenium has been concluded after four years of experimental work. The first two years' work was summarized in WADC TR 54-371, dated June, 1954. The present final technical report covers the period from June, 1954, to June, 1956.

WADC TR 54-371 reported results which were the basis for the experimental work discussed herein. Rhenium is there described as a dense, hard, high-melting metal, difficult to prepare and consolidate, and fabricable only by cold-working and annealing. It was found to have excellent room- and elevated-temperature strength, and in many instances behaved much like tungsten, as might be expected from its position in the periodic system. However, rhenium differs from tungsten in several important respects. For example, it was found to retain ductility after thermal cycling above its recrystallization temperature and to be highly resistant to the water cycle. Under certain circumstances it appeared to be a more promising electrical contact material than tungsten, although not as good a thermionic emitter. Many of the results obtained suggested that rhenium had an excellent future in electronics and allied fields. However, many important properties needed further study and some had not been investigated at all, so that the experimental work reported here is a direct continuation of the work reported in WADC TR 34-371.

During the last two years of research a new method, which is probably superior to the ammonium perrhenate method, was developed for the preparation of rhenium metal powder. This is the halide process.

As during the first two years, studies of the basic physical, mechanical, and electronic properties of rhenium formed the core of the second half of the program. The electrical resistivity of rhenium was redetermined and firmly established from room temperature to about 2300 C. The specific heat was also studied over this range, and the previous vapor pressure work was reviewed. The thermal emf behavior of Re-Pt alloys was evaluated as was that of rhenium coupled with more refractory metals mentioned below. Tensile properties of thoriated rhenium, rhenium sheet, and rhenium-platinum alloys were evaluated, and the shear modulus and elasticity modulus of pure rhenium were studied. Electron emission by heating thoriated rhenium and by use of the photoelectric threshold of pure rhenium, was also studied.

Manuscript released by the authors in June 1956 for publication as a WADC Technical Report.

Some of the properties investigated were pointed directly toward future industrial use of rhenium. For instance, comparison of known data with the thermal emf generated by the rhenium-platinum thermocouple showed that rhenium-molybdenum and rhenium-tungsten thermocouples should also generate high emfs. The work was confirmed experimentally, and it was also found that the couples generally show a linear increase with increase in temperature. Thermocouples of these elements, or possibly rhenium alloys, should be very interesting, although much development work still remains. Use of rhenium in the electronics field was pointed up by results of a test comparing the stability of rhenium and tungsten wires in contact with Al_2O_3 at 1600 C in vacuum. Both metals lasted over 7000 hours to the end of the test, but the tungsten was seriously attacked by water cycling. It was also verified that rhenium does not form a carbide. When rhenium and tungsten wires were exposed to a carbonaceous atmosphere, the tungsten became brittle because of carbide formation, while the rhenium appeared to retain its original ductility.

Rhenium shows good resistance to attack by molten metals except for iron and nickel. Nevertheless, one industrial concern is utilizing rhenium as an evaporation filament for silver and nickel. Results of other industrial work with rhenium are also given in this report.

Most of the properties obtained indicate that rhenium is a metal of considerable interest, with a promising future. However, its scarcity and high cost dictate that any application of the metal must meet two conditions:

(1) The application must require only small quantities of rhenium per unit item.

(2) Rhenium must be critical in the application. That is, it must perform appreciably better than competing materials.

The use of rhenium in electronics and in electrical contacts fits these requirements very well. Development work in the latter field, initiated by information reported in WADC TR 54-371, has been taken up by P. R. Mallory & Co. of Indianapolis, Indiana.

The Chase Brass and Copper Company, which kindly furnished the rhenium used in these investigations, has been developing commercial methods of producing the metal in the common fabricated forms for use in the electrical and electronics fields. Thus the metal appears to be well launched as a new material of technology. However, much more research and development is needed before rhenium's potential usefulness is realized.

METAL PREPARATION, CONSOLIDATION, AND FABRICATION

Preparation of Rhenium Metal Powder

The main objective of this phase of the investigation was to prepare high-purity rhenium powder for subsequent consolidation by powder metallurgy methods. It had been previously determined that rhenium powder prepared by the hydrogen reduction of potassium perrhenate was unsuited for fabrication because of the presence of residual potassium oxide. Conversion of potassium perrhenate to ammonium perrhenate[1], followed by hydrogen reduction of the ammonium perrhenate, yielded a powder which was very low in potassium and which could be successfully pressed and sintered. This method of preparing rhenium metal powder was investigated further, and other new methods were investigated also. The sections immediately below describe the ammonium perrhenate method, various grinding and purifying procedures investigated, and the best method evolved, the halide method of producing rhenium metal.

Rhenium Metal From Ammonium Perrhenate

One difficulty of the ammonium perrhenate method is the necessity of grinding the crystalline ammonium perrhenate to a particle size of less than 325 mesh in order to produce metal powder fine enough for sintering. The comminution is carried out in a rubber-lined ball mill using "Burundum" balls. The initial impurity pickup from this grinding operation is low but, after the Burundum[a] balls became slightly worn, the ammonium perrhenate picks up approximately 0.15 per cent impurities during grinding. These impurities apparently reduce the sinterability of the resulting rhenium metal powder. Other methods, both chemical and mechanical, for reducing the particle size of purified ammonium perrhenate were therefore investigated.

The first chemical method consisted of precipitating ammonium perrhenate from saturated aqueous solutions by lowering the solubility of ammonium perrhenate through the addition of soluble organic liquids, including methyl alcohol, ethyl alcohol, and acetone. This process was tried at temperatures of 25 C and 4 C. At 25 C, the solution became milky in color but the crystals were so fine that none settled out. At 4 C, precipitation of some coarse ammonium perrhenate (about 200 mesh) occurred. This work indicated that precipitation of ammonium perrhenate of the desired particle size probably could be accomplished by this method at a temperature

(a) Approximately 91% Al_2O_3; balance CaO, B_2O_3 and MgO.

between 4 and 25 C, but that recovery would be very low. The maximum recovery was only about 10 per cent, obtained at the lowest temperature, where the ammonium perrhenate was too coarse to be satisfactory.

Improvement in the mechanical methods of reducing the particle size of purified ammonium perrhenate was attempted by modifying the equipment used for ball milling. Tungsten carbide rods were substituted for the Burundum balls used previously. A small 1-quart rubber-lined ball mill was charged with about 100 1/2 by 1/2-inch rods and 100 1/4 by 1/4-inch rods of tungsten carbide. This charge of rods was tumbled in the mill in a solution of commercial detergent for 5 days in order to round off the sharp edges of the rods and to remove irregularities in the rubber lining. Then 50 grams of crystalline ammonium perrhenate was ground in the mill for 1 hour to break it in. The fine perrhenate was removed and reprocessed.

After this preparatory work, one pound of ammonium perrhenate was ground in the mill for 1-1/2 hours. Almost all the resulting perrhenate was of the desired particle size (-325 mesh) and the entire lot of material was used without screening. An analysis of the fine ammonium perrhenate (see Table 1) indicated the presence of 0.25 per cent tungsten. While the pickup of tungsten from tungsten carbide rods was of the same order of magnitude as the pickup of impurities from Burundum balls, the tungsten carbide impurity had little noticeable effect on the densification of the powder during sintering operations. It was expected that with additional use of the mill the tungsten carbide impurity in the ground perrhenate would decrease.

No further work was done by this method, however, because, for reasons not determined, the potassium content in the ammonium perrhenate progressively increased with succeeding batches to a value of 0.47 per cent. When this perrhenate was reduced to the metal, it contained 0.40 per cent potassium, approximately the same amount as that found in metal produced by the hydrogen reduction of potassium perrhenate. As previously stated, the fabrication by powder metallurgy techniques of rhenium powder prepared from potassium perrhenate was unsuccessful.

Two different methods of purifying this metal were tried: (1) leaching with dilute hydrochloric acid followed by leaching with distilled water, and (2) conversion of the metal to the pentachloride, followed by hydrolysis of the chloride to produce rhenium dioxide. Leaching was not effective in further purifying this metal. However, the chloride or halide method, which is described in detail in the following section, produced high-purity oxide from which high-purity metal was obtained by hydrogen reduction.

Rhenium Metal by the Halide Method

Rhenium metal obtained from potassium perrhenate, ammonium perrhenate, or scrap massive rhenium (see Figure 1) was placed in a Vycor reactor 2 inches I. D. x 6 inches long (see Figure 2) and heated to 1000 C in a hydrogen atmosphere to assure that all the rhenium was reduced to the metal. The reactor was cooled to 750 C in a helium purge and held at this temperature for 1 hour in order to assure the complete removal of any hydrogen. The helium purge was shut off and sufficient tank chlorine was passed through the charge to keep a slight positive pressure on the exit line. The chloride was condensed in an air-cooled trap. Under these conditions, rhenium metal was chlorinated to rhenium pentachloride at the rate of about 150 grams per hour.

When the chlorination was completed, the chloride was hydrolyzed by adding it cautiously to distilled water cooled to about 10 C in an ice bath. The main product of the hydrolysis was finely divided hydrated rhenium dioxide. Perrhenic acid and chlororhenic acid were also formed in smaller amounts. In cold water, approximately 75 per cent of the available rhenium was recovered as rhenium dioxide. If the hydrolysis is not carried out in cold water, the yield of rhenium dioxide is somewhat lower. The hydrated oxide had the consistency of a gel and was quite difficult to filter. However, bubbling carbon dioxide through the hydrolysis products for approximately 1/2 hour reduced the filtration time by as much as 94 per cent.

The hydrated rhenium dioxide was filtered off or separated from the liquor by centrifuging, washed several times with distilled water, and dried in a vacuum desiccator.

The bulk of the rhenium, as ReO_2, was reduced to metal by hydrogen, by exposing a 1/2-inch layer of ReO_2 in a molybdenum boat to hydrogen for one hour at 400 C and for a second hour at 600 C. The rhenium metal produced was loosely sintered and was broken up in an agate mortar and again treated with hydrogen at 800 C for two hours. The charge was then cooled to room temperature in an inert or reducing atmosphere.

To recover the rhenium from the filtrate, a small amount of 30% hydrogen peroxide was added to the solution to convert all the rhenium present to perrhenic acid. The perrhenic acid was neutralized by the addition of ammonium hydroxide and the resultant ammonium perrhenate filtered off and reduced to the metal by hydrogen.

A typical analysis of rhenium powder prepared by the halide process is given in Table 1 along with the analysis of rhenium prepared from potassium perrhenate and ammonium perrhenate. The over-all rhenium recovery efficiency was about 95 per cent.

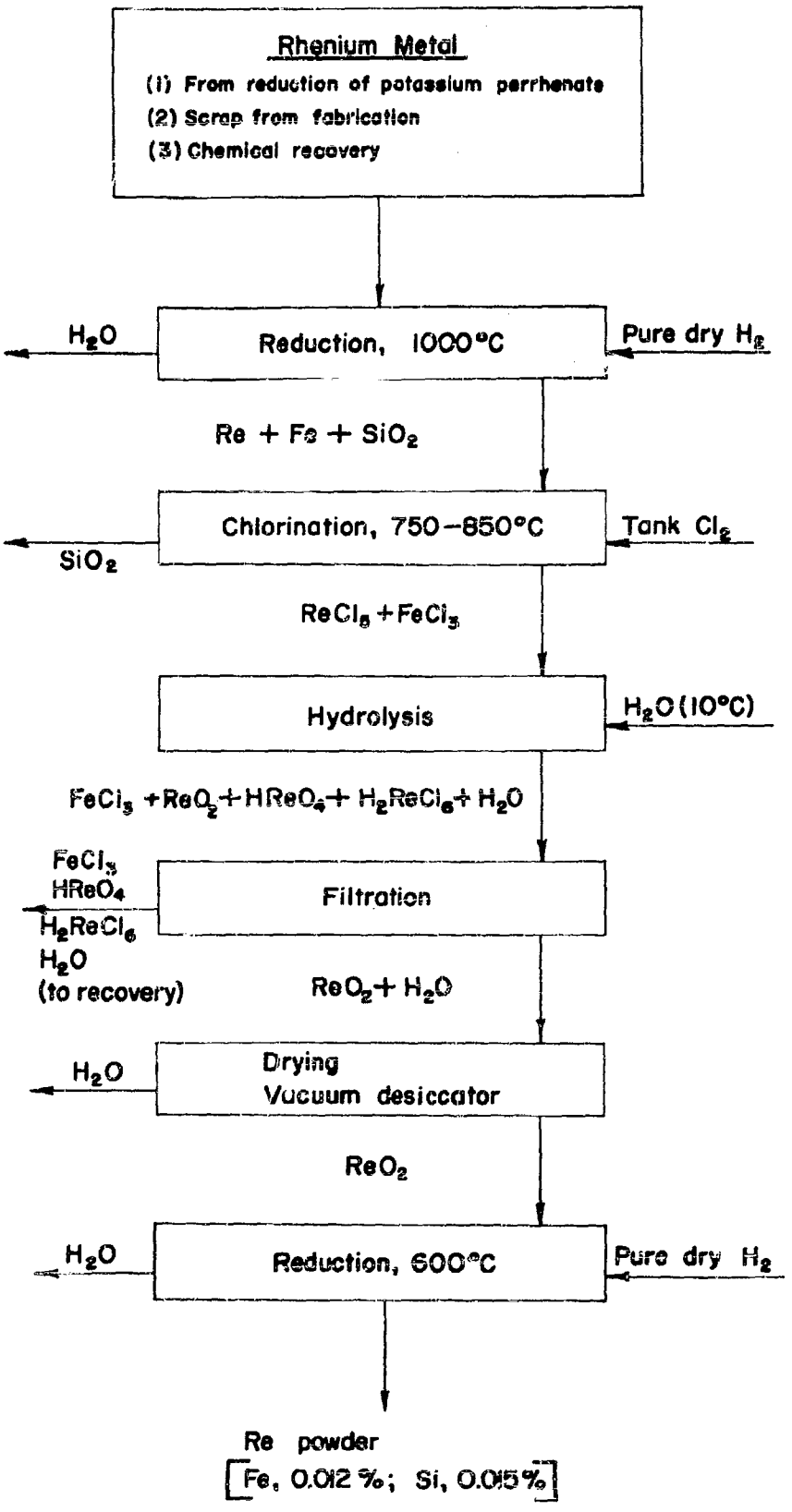

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FIGURE 1. SCHEME FOR THE PREPARATION OF RHENIUM METAL BY HYDROLYSIS OF A VOLATILE HALIDE

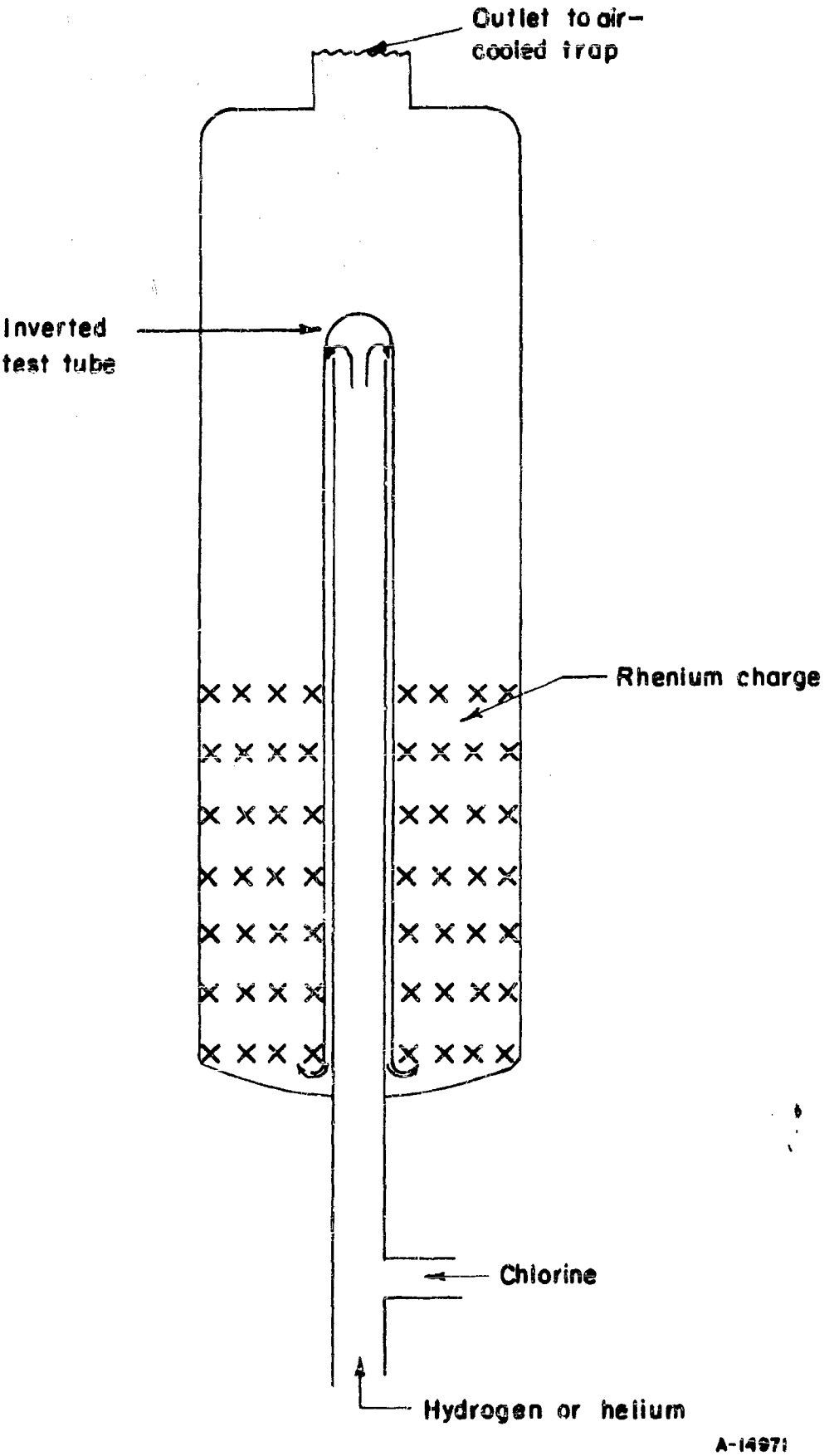

FIGURE 2. APPARATUS FOR CHLORINATION OF RHENIUM

TABLE 1. TABLE OF ANALYSES

Element	Weight Per Cent			
	Rhenium Metal Prepared From Potassium Perrhenate	Rhenium Metal Prepared From Ammonium Perrhenate(1)	Rhenium Metal Prepared From Ammonium Perrhenate(2)	Rhenium Metal Prepared By The Halide Method
Aluminum	0.009	0.094	0.002	0.008
Calcium	0.008	0.017	0.005	0.002
Chromium	0.004	N.F.*	N.F.	N.F.
Copper	0.0012	0.0021	0.0008	0.0002
Iron	0.05	0.024	0.010	0.012
Magnesium	0.002	0.038	0.003	0.005
Manganese	0.007	0.002	N.F.	0.007
Molybdenum	0.15	N.F.	N.F.	N.F.
Nickel	0.003	N.F.	0.002	N.F.
Potassium	0.41	N.F.	(0.40)3	N.F.
Rhenium	Major	Major	Major	Major
Silicon	0.005	0.028	0.125	0.015
Sodium	0.15	N.F.	N.F.	N.F.
Tungsten	N.F.	N.F.	0.25	N.F.
Total	0.799	0.205	0.398	0.049

*N.F. = Not found.

(1) Ground with "Burundum" balls.

(2) Ground with tungsten carbide rods.

(3) The value of potassium listed is a result of an impurity in the ammonium perrhenate and was not an impurity picked up during grinding operations. This value gradually increased with subsequent batches of ammonium perrhenate to the reported value. The halide method was then used for the preparation of rhenium metal. The potassium content of 0.40 per cent is not included in the total impurity value of 0.398 per cent.

Elements checked for but not found: antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, cobalt, columbium, gallium, germanium, gold, lead, platinum, silver, strontium, tellurium, tin, titanium, vanadium, zinc, and zirconium.

The halide process has several advantages over the other processes:

(1) The metal prepared is higher in purity than that obtained by the other processes; in particular, it is free of potassium.

(2) The particle size of the metal powder prepared by the halide method is such that it can be sintered satisfactorily and no comminution is necessary.

(3) The halide method involves substantially fewer steps than the ammonium perrhenate method.

Details of the fabrication of halide metal are discussed in the following part of this report.

Fabrication of Halide-Process Rhenium

Rhenium metal powder prepared by the halide process was consolidated and worked successfully to rod, wire, and sheet. The metal was pressed, sintered, and fabricated by the processes described in detail previously[1]. The halide-process rhenium metal powder pressed to more dense compacts than the metal powder produced by hydrogen reduction of ammonium perrhenate, but did not sinter to as high density. It was previously determined that the perrhenate-type metal can be pressed (at 30 tsi) to densities of about 40 per cent of ideal density, and sintered (at 2700 C) to 90 per cent of ideal density. The halide-process rhenium can be pressed to 60 per cent but sintered to only 80 per cent of ideal density under the same conditions. Although a sintered density of about 90-95 per cent of ideal is desirable, the halide-process metal is still capable of fabrication to sheet and wire with careful handling.

Further study of rhenium prepared by the halide process is needed, since the metal prepared by this process is of higher purity and the preparation scheme is less costly than in the earlier processes. The poor densification achieved by hydrogen sintering is probably abnormal and due to a controllable secondary factor such as excessive surface oxide on the metal powder particles.

Fabrication of Perrhenate-Process Rhenium

During the two years' work covered by this report, several pounds of rhenium metal in rod, wire, sheet, and foil form were prepared by reduction

of ammonium perrhenate. The procedures used to fabricate this metal have been described in detail previously[1], and involve cold working and annealing of metal bars consolidated by powder metallurgy techniques. Rhenium can not be hot worked because of hot shortness. However, the cold-working and annealing procedure for reduction of rhenium to final fabricated form is quite laborious and time-consuming, so that several short investigations were undertaken to attempt to improve the situation. These studies are discussed below, together with the results of fabrication studies on the preparation of fine wire and foil.

Hot Swaging

A specimen of high-purity rhenium containing about 0.09 per cent total impurities[a] was swaged hot in air from a hydrogen-atmosphere furnace to establish whether its lower impurity content would result in improved hot workability. The hydrogen furnace temperature was 1700 C. Four swaging passes were made, each at a reduction in cross-sectional area of 10 per cent. After the first pass, a longitudinal crack appeared. After the second pass, the surface hardness was nearly 700 VHN; therefore a 2-hour anneal at 1700 C was given. After the fourth pass, the bar was badly cracked and the experiment was halted. It was obvious that rhenium of improved purity is also hot short. No further attempts to hot swage rhenium were made.

Cold Rolling

Previous data[1] show that it is possible to reduce sintered rhenium to strip about 8 mils' thickness in a two-high rolling mill with rolls 3-1/2 inches in diameter and 6 inches long. Reduction was of the order of only 0.001 inch per pass when a thickness of 10 mils was reached, and considerable intermediate annealing was necessary to secure reduction to 8 mils.

During the present report period, further rolling was done in a four-high Waterbury-Farrell semiautomatic foil mill with 2-inch work and 6-inch backup rolls. Reduction was much more rapid in this mill, and, in only 5 to 12 passes, 5- and 3.5-mil strip foil was prepared from the 8-mil stock. The metal was flat, had an excellent surface, and was almost without edge cracks in the finished condition. No reduction below 3.5 mils was attempted.

Fine Wire Drawing

Previously, no attempt had been made to prepare wire under 10 mils in diameter. However, demand by industry for samples of sub-10-mil sizes

(a) Rhenium prepared in this work normally contained about 0.2 per cent total impurities (see Table 1).

was persistent, and it was felt that the finer stock should be prepared. This would also establish the feasibility of fine wire drawing in general.

Rhenium containing 0.5 per cent thoria, previously prepared for electronic studies and available at 20 mils diameter, was used for this purpose. It was found that below 15 mils diameter two 10 per cent reductions could be taken between anneals. Diamond dies were used from 10 mils down to 2.9 mils, the smallest diameter of wire prepared. Houghton's Cyl-Tal No. 81 was used as drawing lubricant. The 2.9-mil wire appeared satisfactory, although microinspection indicated some surface pitting. Dies are not available for drawing below 2.8 mils, but it is believed that finer sizes could have been prepared.

Fabrication Comparison of Thoriated and Nonthoriated Rhenium

Recrystallization data on thoriated rhenium[1] indicate that thoria lowers the recrystallization temperature. Laboratory experience also indicates thoriated rhenium is annealed much more readily than pure rhenium. Therefore, it was decided to conduct studies on the use of thoria to improve fabrication. 0.75 per cent thorium was uniformly dispersed in rhenium powder by adding a water solution of $Th(NO_3)_4$, converting to $Th(OH)_4$ by dropwise addition of NH_4OH, drying, and sintering. During sintering, the $Th(OH)_4$ was in all likelihood converted to ThO_2. Next, the bar was fabricated by swaging. For comparison purposes, another bar, containing no thoria, was simultaneously prepared from the same lot of rhenium powder and fabricated by swaging. Vickers hardness measurements were taken before and after each working pass on the surface of each bar.

Generally, the pure rhenium maintained hardnesses below those for the thoriated specimen, although there were some exceptions. After 70 per cent total reduction, the differences in hardnesses for thoriated and unthoriated rhenium were insignificant. The thoriated rhenium was then drawn to 0.016-inch wire by 10 per cent reductions between anneals. This was done only with difficulty, however, since the thoriated wire was much more liable to break during drawing than pure rhenium was. The thoriated wire contained many surface imperfections, consisting mainly of longitudinal fissures. Far from enhancing fabricability, it is probable that thoria additions reduced it.

PHYSICAL PROPERTIES

Electrical Resistivity

The electrical resistivity of rhenium had been studied previously[1], but disagreement in the data and the importance of this property to the applications of rhenium made redetermination essential. Accordingly, electrical resistivity as a function of temperature was redetermined experimentally in four distinct steps. First, the room-temperature resistivity was established by two separate measurements on a length of high-purity 50-mil wire as reported in detail below. The resistivity between room temperature and 725 K was determined with the rhenium wire in an evacuated tube. Heating was accomplished in a large muffle furnace and temperature measured by thermocouples. The wire was mounted in the open in a hydrogen atmosphere furnace, for measurement of the resistivity from 725 K to 1100 K. Temperature measurement was also by thermocouple. The same wire was also mounted in an evacuated tube for resistivity determinations at elevated temperatures from 1100 to 2700 K. In this case, heating was by self-resistance, and temperature was measured optically.

Following these measurements, the wire was sectioned and chemically analyzed. It contained approximately 0.06 per cent total impurities as shown in Table 2. A drawing of the vacuum apparatus used for two of the four series of resistivity determinations is given in Figure 3. Discussion of the individual resistivity experiments, in order of increasing temperature, follows.

Preparation of Resistivity Specimen

The rhenium metal was prepared from ammonium perrhenate which had been ground by hand in an agate mortar to insure minimum impurity pickup. The consolidated metal was reduced by swaging and wire drawing to a diameter of about 50 mils, and then annealed at 1750 C for 2 hours.

Resistivity at Room Temperature

A Kelvin bridge was used for the room-temperature measurements. The resistance was measured for a length of 14.90 cm for each test, and all readings were taken at 77 F in a constant-temperature room. About 50 individual micrometer measurements were averaged to give the wire diameter [0.0518(9) inch]. The resistivity was then calculated from the resistances found on the Kelvin bridge by the well-known relationship:

TABLE 2. SPECTROCHEMICAL ANALYSIS OF RHENIUM RESISTIVITY SPECIMEN[a]

Impurity	Per Cent by Weight
Copper	0.0005
Tin	0.014
Aluminum	0.015
Silicon	0.010
Magnesium	0.005
Calcium	0.010
Molybdenum	0.004
Gold	0.0X
Total	0.0585 (plus gold)

(Elements checked but not found: As, Sb, Ba, Be, Bi, B, Cd, Cr, Co, Ga, Ge, Pb, Mn, Nb, Ni, Pt, K, Ag, Na, Sr, Te, Ti, W, V, Zn, Zr)

(a) Analysis by W. B. Coleman & Co., Philadelphia, Pennsylvania.

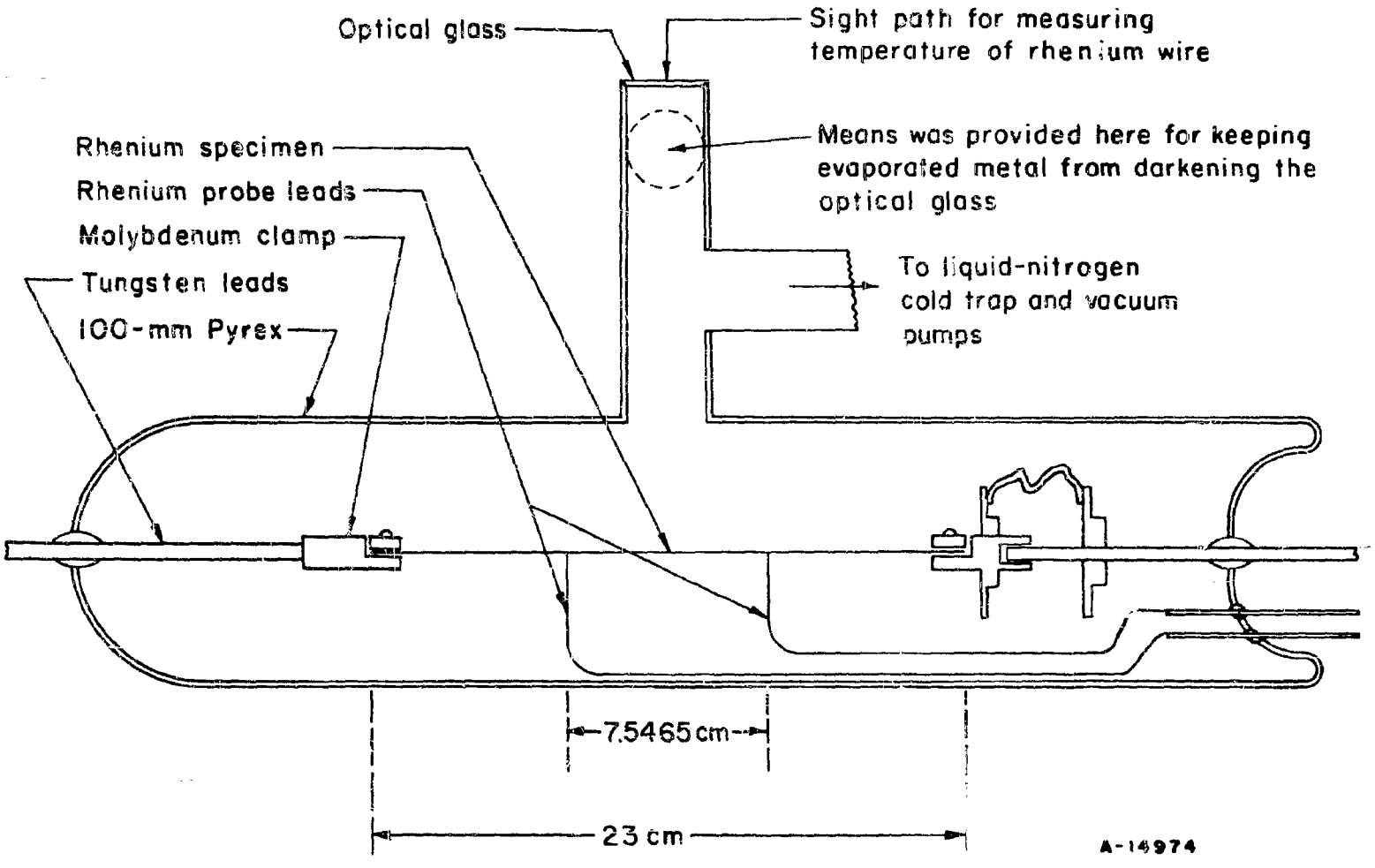

FIGURE 3. SCHEMATIC DRAWING OF THE VACUUM CHAMBER EMPLOYED FOR THE RHENIUM RESISTIVITY MEASUREMENTS

$$\rho = \frac{RA}{\ell},$$

where

ρ = resistivity, ohm-cm

R = resistance, ohms

A = cross-sectional area, cm^2

ℓ = length, cm

Resistance readings were taken at several different times following the initial 2-hour anneal. More anneals, followed by resistivity determinations, were taken until the resistivity leveled off. A relatively level series of readings was reached after 3 hours of annealing; therefore the resistivity values directly after 2 hours' annealing time were discarded. Two readings were made after 3 hours and two more after 4 hours' total annealing time. All of these values and additional readings at 5, 6, and 7 hours' annealing time were then averaged, giving a calculated resistivity of 19.50 ± 0.01 microhm-cm (at 77 F, or 25 C).

This value was plotted with the low-temperature resistivity data shown in Figure 4, and the curve extrapolated through 20 C. The resistivity value at 20 C was 19.3 microhm-cm as read from the curve. This is the most accurate value of the resistivity at 20 C found in the present work.

Resistivity From Room Temperature to 725 K (452 C)

The 51-mil wire used for the room-temperature measurements was used also for the determinations from room temperature to 725 K, although chronologically the measurements from 1100 K to 2700 K reported below were made directly following the room temperature measurements.

The variation of resistance with temperature in a 7.1140-cm portion of the wire was measured utilizing the apparatus shown in Figure 3, except that the sight tube shown was replaced with sealed thermocouple leads. A Chromel-Alumel thermocouple was mounted so that the bead lightly touched the center of the rhenium wire. The apparatus was heated from 300 to 700 K in a large muffle furnace. The resistance of the known length of wire was measured on a Kelvin bridge, and the temperature at the wire was recorded by the Chromel-Alumel thermocouple at temperature intervals of about 25 K. The resistivity values calculated from these data are reported in graphical form in Figure 4.

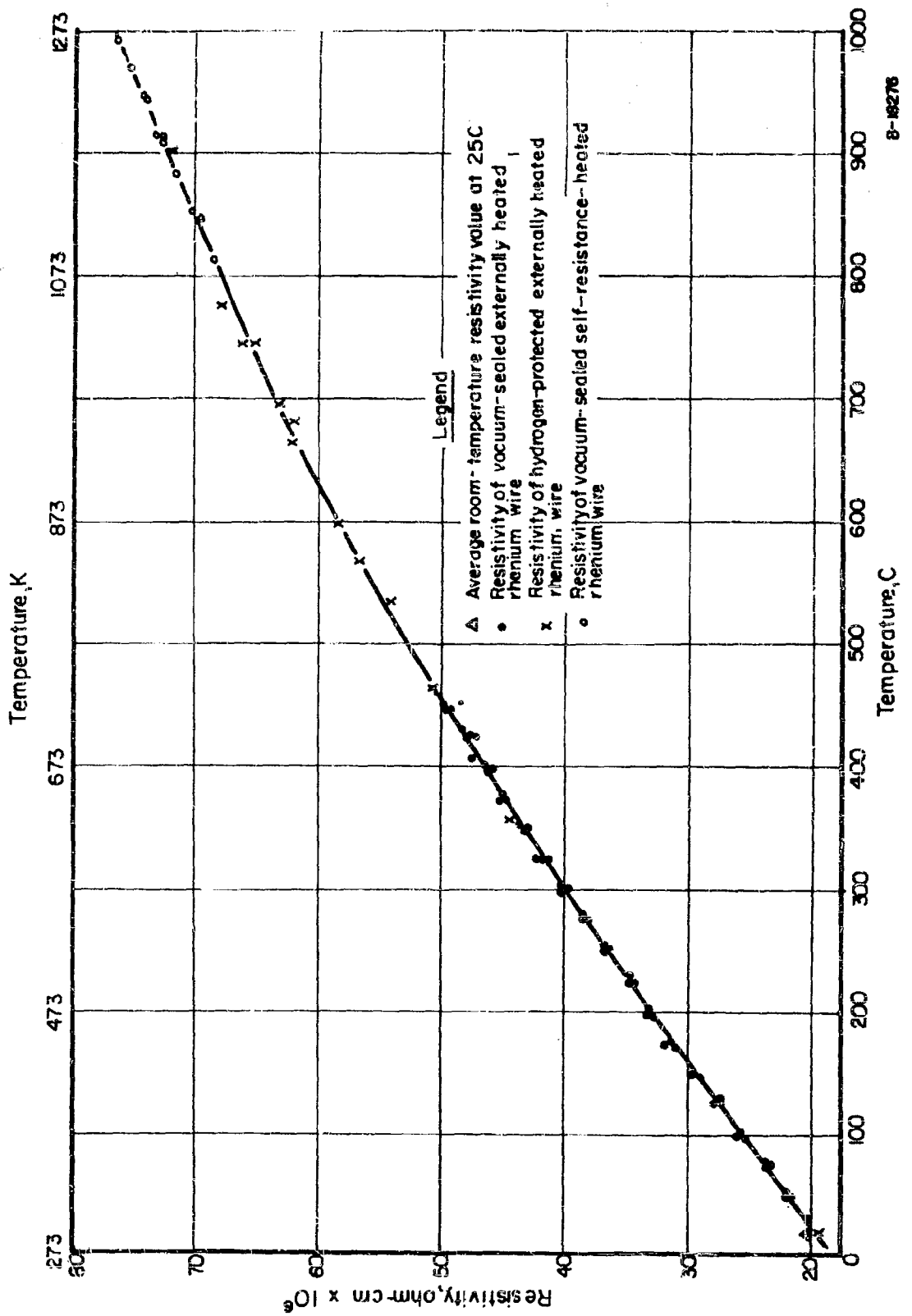

FIGURE 4. ELECTRICAL RESISTIVITY OF RHENIUM FROM ROOM TEMPERATURE TO 1273 K (1000 C)

Resistivity From 629 K (356 C)
to 1175 K (902 C)

The range from 629 K to 1175 K is the most difficult temperature range to evaluate for resistivity. Since it is above the softening point of Pyrex, the vacuum-sealed apparatus of Figure 3 cannot be furnace heated. On the other hand, the temperature range is below the useful range of optical pyrometers, so that self-resistance heating with a sealed unit cannot be used. Attempts to heat by self-resistance and to measure the temperature by a thermoelement welded to the wire were also unsuccessful, because the current used for heating the rhenium specimen caused severe errors in the thermocouple readings.

Finally the 51-mil specimen was removed from the vacuum-sealed Pyrex tube, mounted in an open alumina boat, and fitted with the proper leads for Kelvin bridge resistance measurements. Two Chromel-Alumel thermocouples were mounted so that the hot junctions touched or were in very close proximity to the rhenium wire at the center of the test portion. The apparatus was inserted into a hydrogen-atmosphere molybdenum-wound tube furnace and resistance readings taken over the desired temperature range. Different resistance values were found when the leads to the rhenium probes were reversed at the Kelvin bridge terminals. This may have been due to a temperature gradient in the wire, resulting in a thermocouple effect. To minimize this effect, two resistance readings were taken at each temperature with the leads reversed. The resistance readings were then averaged. Any temperature gradient existing in the wire was assumed to be uniform. Resistivity values calculated by this procedure are plotted in Figure 4, and fall on a smooth curve connecting the low-temperature and high-temperature values determined by other methods. Thus, the assumption that a uniform temperature gradient existed in the wire appears to be correct, within the accuracy limits of the plot in Figure 4.

Resistivity From 1100 K (827 C)
to 2050 K (1770 C)

To determine resistivity from 1100 K to 2050 K the resistance of a measured length of the rhenium specimen was determined from the voltage and the direct current through the measured length. In most of these measurements, the voltage was measured with a Leeds & Northrup Type K_2 potentiometer, although for a few measurements, the voltage was determined with an SIE Model P2 potentiometer. The current was determined by measuring the voltage across a Leeds & Northrup standard resistor (L & N No. 4363) placed in series with the rhenium wire. When two Type K_2 potentiometers were employed, they were balanced simultaneously and standardized from the same standard cell. A schematic diagram of the electrical-measurement apparatus is shown in Figure 5. The temperature

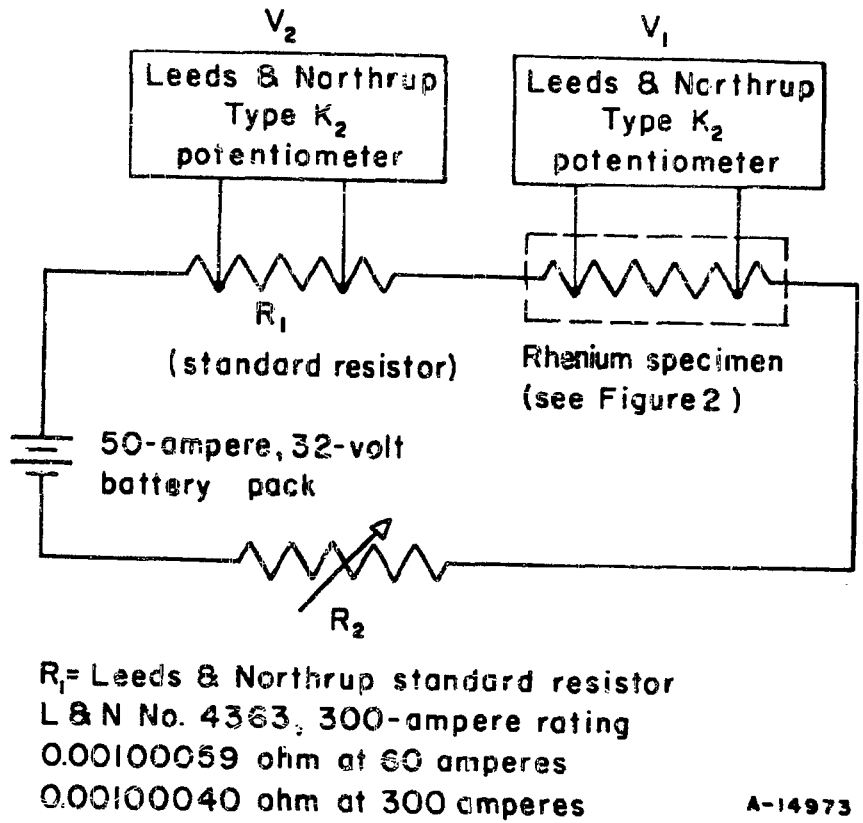

FIGURE 5. SCHEMATIC DRAWING OF ELECTRICAL APPARATUS FOR DETERMINING ELECTRICAL RESISTIVITY OF RHENIUM

was measured with a Leeds & Northrup optical pyrometer. An average was taken of several temperature readings by two observers.

The vacuum chamber and the mechanical structure of the resistivity apparatus are shown in Figure 3. The rhenium wire was supported by molybdenum clamps, which in turn were connected to tungsten leads. The resistivity was ultimately determined from the voltage measurements and from the physical dimensions for a 7.5465-cm-long center section of the 23-cm long rhenium wire. The diameter of the wire was 0.1316 cm. A temperature gradient within the sensitivity of the optical pyrometer was not detected at 2500 F.

From the dimensions of the wire specimen and the value of the standard resistor, the resistivity is calculated from the equation:

$$\rho = 1.8024 \frac{V_1}{V_2} \text{ microhm-centimeter} ,$$

where V_1 is the potential in volts across the rhenium specimen, and V_2 is the potential in volts across the standard resistor. The value of the standard resistor, as certified by the National Bureau of Standards, is 0.0010059 ohm absolute at 25 C while passing 60 amperes. Sixty-five resistivity determinations were made within the stated temperature range. The spectral emissivity (at $\lambda = 0.655\mu$) was taken from earlier work on this project as equal to 0.42, over the temperature range employed. The resistivity as a function of temperature in this temperature range is given in Figure 6.

Resistivity From 2000 K (1727 C)
to 2700 K (2427 C)

For the range from 2000 K to 2700 K, the resistance of a measured length of the rhenium specimen was determined, as before, from the voltage across and the d-c current through the measured length. A battery power source was not available that would supply sufficient d-c current for temperatures above about 2000 K, so that it was necessary to employ a d-c source consisting of a generator-battery combination. The voltage fluctuations of this source were, of course, greater than those in the simple battery supply that was employed for the resistivity measurements below 2000 K. In most of these measurements, the voltage was determined with a Weston 1/2 per cent voltmeter, although for a few measurements a Southwestern Industrial Company Model P-2 potentiometer was used. The current was determined by measuring the voltage across a Leeds and Northrup standard resistor (L & N No. 4363) placed in series with the rhenium wire. An L & N Type K-2 potentiometer was employed for this measurement. The apparatus was identical with that shown in Figures 3 and 5 except for the voltage source and voltmeters. The temperature was measured with a Leeds and Northrup optical pyrometer. An average was taken of several readings at each temperature.

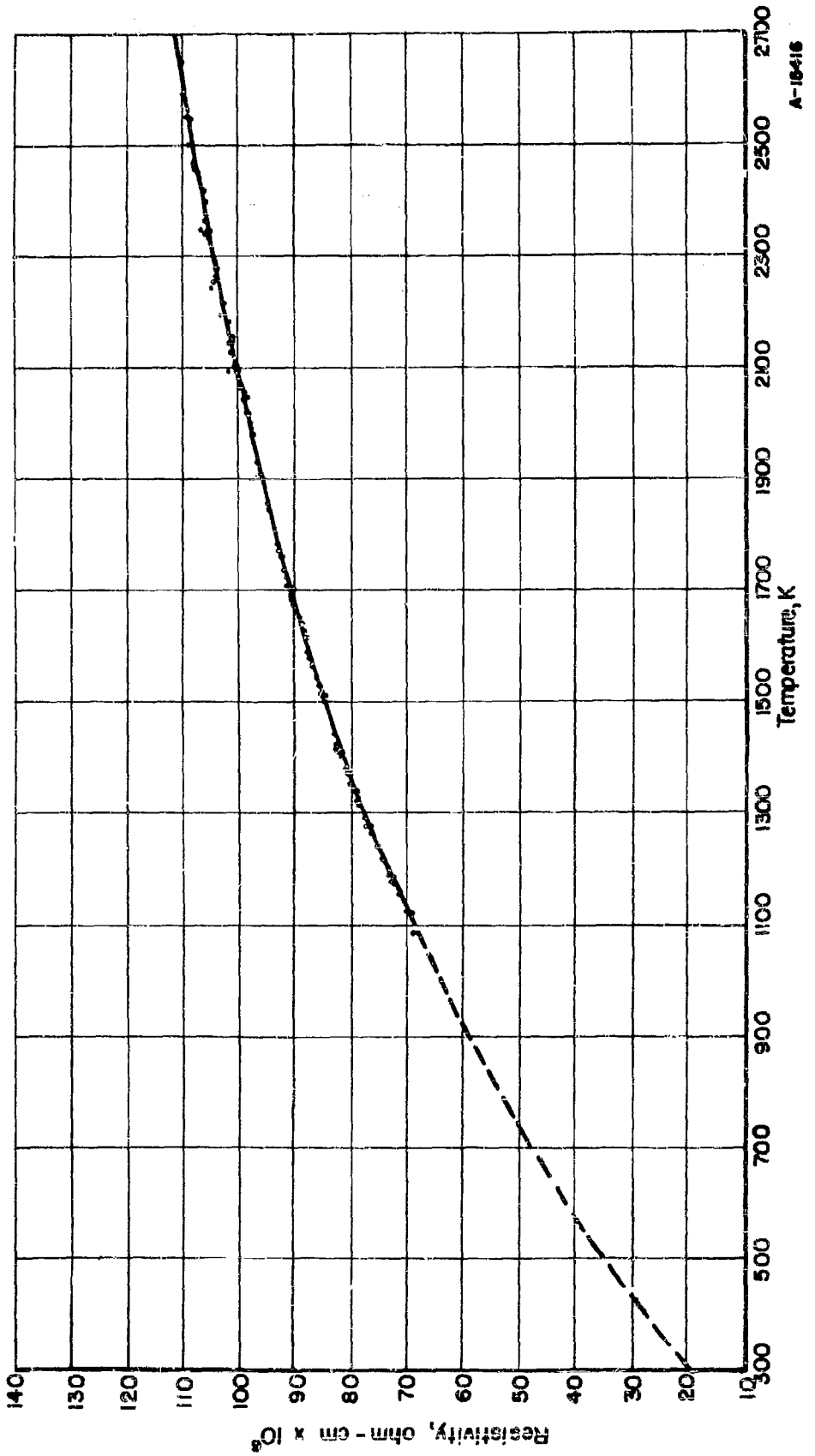

FIGURE 6. ELECTRICAL RESISTIVITY OF RHENIUM FROM 1100 K (827 C) TO 2700 K (2427 C)

From the dimensions of the wire specimen and the value of the standard resistor, the resistivity of rhenium is calculated from the equation,

$$\rho = 1.8024C \frac{V_1}{V_2} \text{ microhm-centimeter,}$$

where V_1 is the potential in volts across the rhenium specimen, V_2 is the potential in volts across the standard resistor, and C is a correction factor, the meaning of which is discussed below.

At the very high temperatures reported here, the evaporation of the rhenium causes a noticeable change in the resistivity measurements. The data were corrected for the resulting change in diameter by employing the known resistivity values for the temperature range 1100 to 2000 K, where evaporation is not significant. The procedure for determining this correction was as follows: The rhenium wire was raised to a high temperature, and the current through the wire and the voltage across the measured length were determined with as little loss of time as possible. Immediately after these measurements, the temperature was dropped to below 2000 K to reduce evaporation. Several measurements were then taken in the temperature range from 1100 to 2000 K and a smooth curve was drawn through these points. From this curve and the known relationship between resistivity and temperature within this range determined previously, the change in diameter was determined. This is the value of C in the equation above. This procedure was repeated until a number of corrected resistivity determinations had been made in the temperature range from 2000 to 2700 K.

The values of resistivity as a function of temperature at the very high temperatures are plotted in Figure 6, along with the values for temperatures between 1100 and 2050 K. Scatter in the data is primarily due to voltage fluctuations in the d-c power source.

Summary of the Resistivity Data

All of the electrical resistivity data at various temperatures have been plotted on a single graph, and a resistivity vs temperature curve drawn from room temperature to 2700 K. This curve, without the specific data points so as to give greater clarity, is given in Figure 7.

In addition, a mathematical expression of the power series type has been developed relating the electrical resistivity to absolute temperature as follows:

$$\rho = -4.50 + 9.00 \times 10^{-2}T - 2.35 \times 10^{-5}T^2 + 2.2 \times 10^{-9}T^3 \ ,$$

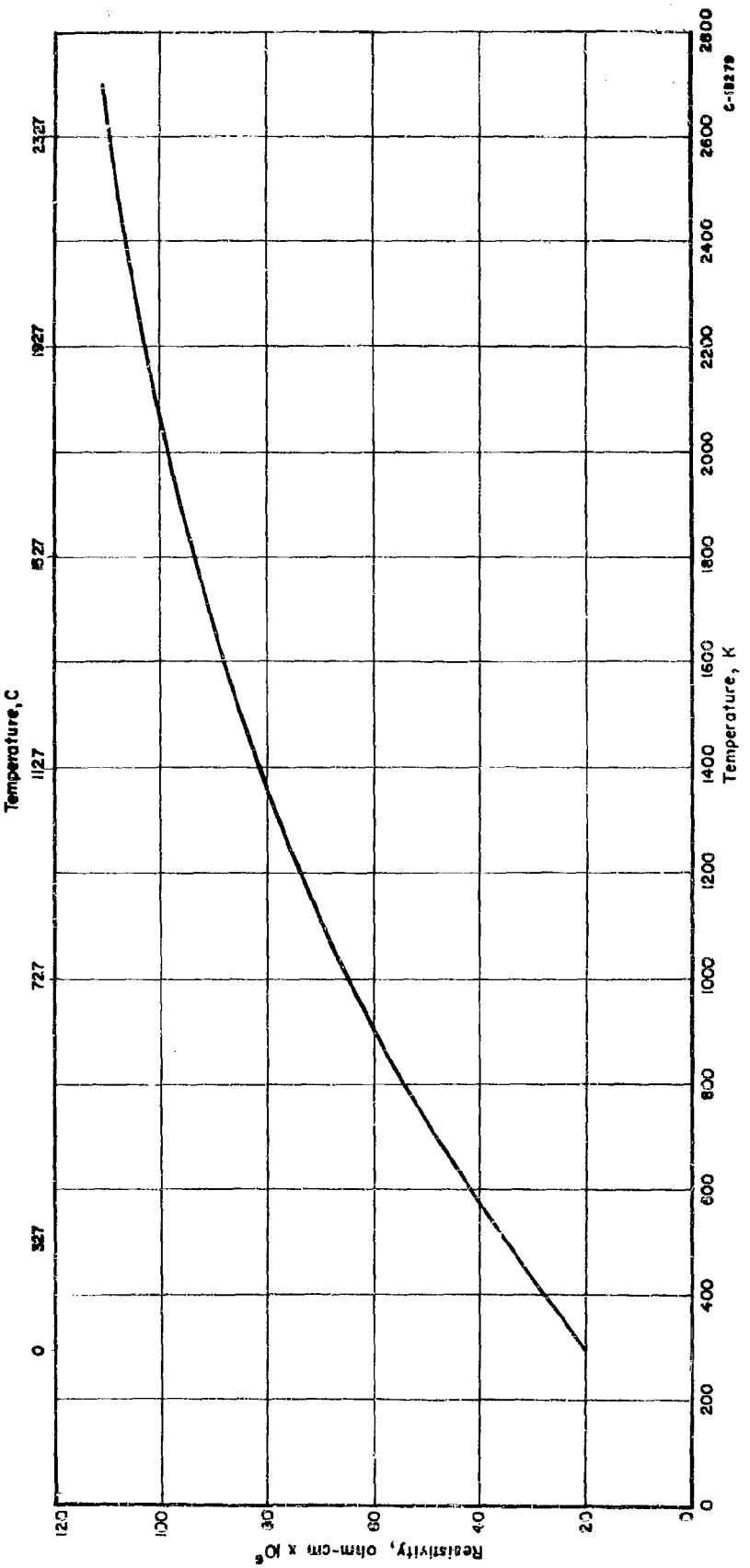

FIGURE 7. AVERAGE PLOT OF THE DATA RELATING ELECTRICAL RESISTIVITY OF RHENIUM TO TEMPERATURE

where

ρ = resistivity, microhm-centimeters

T = absolute temperature, K.

Figure 8 gives the raw data together with a plot of this equation from room temperature to 2400 C. The equation is a good expression for the temperature-dependency of resistivity, particularly above 400 C. However, some deviation occurs between room temperature and about 300 C, and a second equation has been developed for use in this temperature range only as follows:

$$\rho' = -4.50 + 8.20 \times 10^{-2}T - 2.8 \times 10^{-11}T^4 ,$$

where

ρ' = resistivity, microhm-centimeters, from 0 to 300 C

T = absolute temperature, K.

For convenience, values of resistivity have been taken from Figure 4 (room temperature to 300 C) and from Figure 7 (300 C to 2400 C) and summarized in Table 3.

Temperature Coefficient of Resistivity

Agte, et al.[2], has reported the temperature coefficient of resistivity, α, for rhenium from 20 C calculated for several temperatures in the ranges from -190 to 120 C and 2222 to 2712 C. In the present work, the temperature coefficient of resistivity has been calculated for temperatures from 20 C to 2300 C at 200-C intervals. The data are compared to Agte's results in Table 4, where it can be seen that the present work gives higher values near room temperature and lower values at very high temperatures.

Specific Heat of Rhenium

Relative values of the specific heat were determined for the temperature range from 1620 to 2690 K. The specific heat of rhenium has been measured up to 1473 K (1200 C) by Jaeger and Rosenbohm[4]. When employing the calorimetric method, they found the following empirical relationship between the specific heat and the temperature:

$$C_p = 0.03256 + 0.6625 \times 10^{-5}\ t \text{ cal/g/C} . \qquad (1)$$

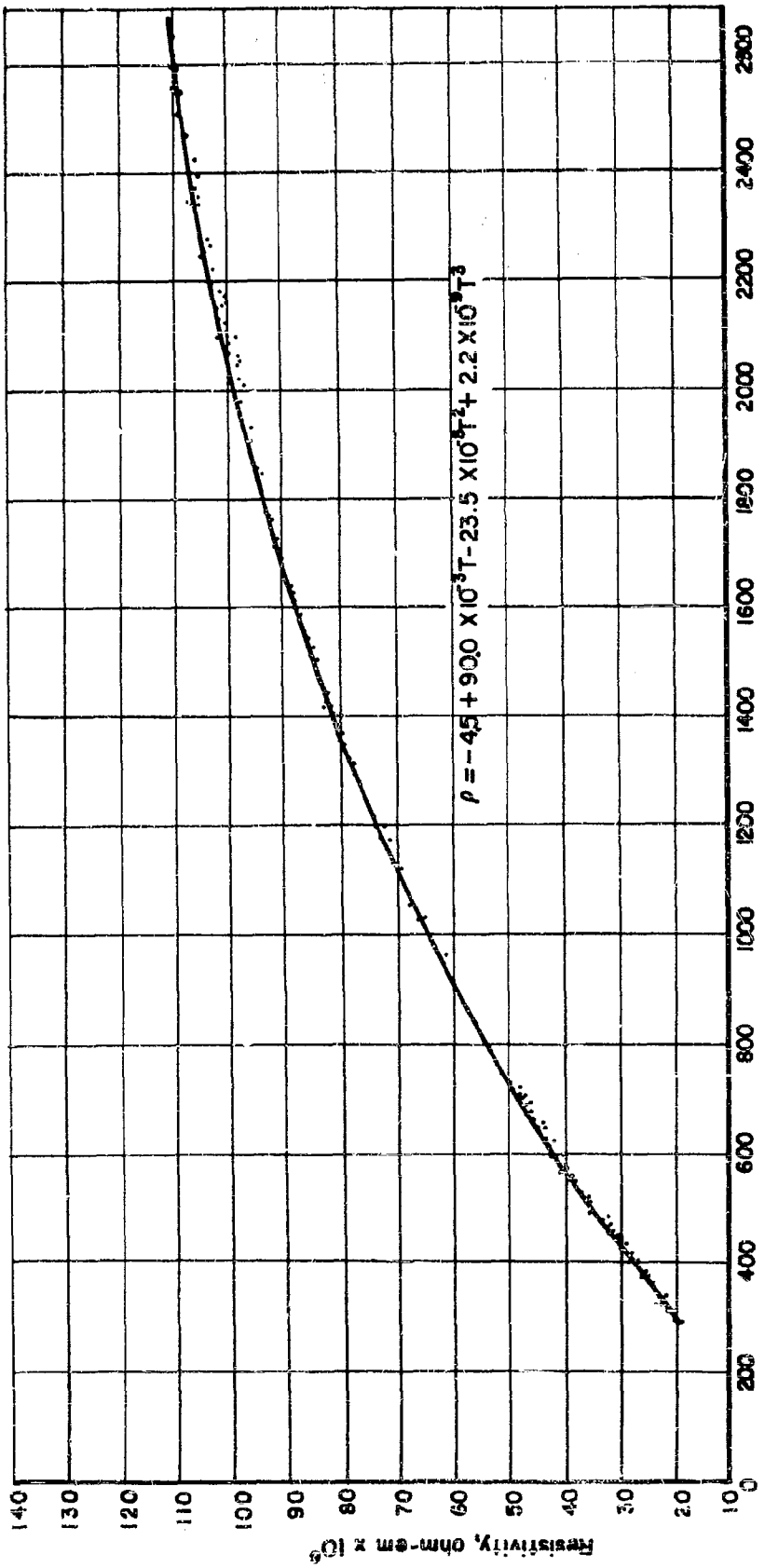

FIGURE 8. ELECTRICAL RESISTIVITY OF RHENIUM AS A FUNCTION OF TEMPERATURE
Raw Data With Plot of a Mathematical Expression

TABLE 3. THE ELECTRICAL RESISTIVITY OF RHENIUM METAL FROM 20 TO 2400 C

Temperature, C	Resistivity, microhm-centimeters
20	19.3
100	25.4
200	32.8
300	40.0
400	46.5
500	52.6
600	58.0
700	63.0
800	67.0
900	72.5
1000	76.5
1100	80.5
1200	84.0
1300	87.0
1400	90.0
1500	93.0
1600	96.0
1700	98.5
1800	101.0
1900	103.0
2000	105.0
2100	106.5
2200	108.0
2300	109.0
2400	110.0

TABLE 4. TEMPERATURE COEFFICIENTS OF RESISTIVITY CALCULATED FROM THE PRESENT WORK AND COMPARED TO THOSE OF AGTE, ET AL.[2]

Temperature, T		Resistivity (ρ), microhm-centimeters		Resistivity-Temperature Coefficient, 1/C $\alpha = \frac{\frac{R_T}{R_{293}} - 1}{T\,(a) - 293} \times 10^3$	
		Present	Agte,		
C	K	Work	et al.	Present Work	Agte, et al.
-190	83		4.94		3.65
-30	243		15.4		3.35
0	273		19.8		3.11
20	293	19.3	21.1		3.11
100	373	25.4		3.95	
120	393		26.1		3.11
300	573	40.0		3.83	
500	773	52.5		3.58	
700	973	63.0		3.33	
900	1173	72.5		3.13	
1100	1373	80.5		2.94	
1300	1573	87.0		2.74	
1500	1773	93.0		2.58	
1700	1973	98.5		2.44	
1900	2173	103.0		2.31	
2100	2373	106.5		2.17	
2222	2495		125		2.23
2300	2573	109.0		2.04	
2417	2690		130		2.14
2712	2985		134		1.98

(a) In degrees Kelvin.

Relative values of the specific heat were determined in this laboratory by a method whereby the heat input is increased in a step. A rhenium wire was heated to each selected temperature by resistance heating with a conduction current. The stepwise increase in heating was obtained by a stepwise increase in the current. From the observed rate of rise of temperature and from the physical constants for rhenium wire, the relative specific heats at different temperatures are readily calculated. At some preselected value of the temperature, T_1, the power input per unit length to the wire, P_1, may be related to the temperature by the expression,

$$P_1 = f_1 (T_1) \quad . \tag{2}$$

If the power is increased to P_2, then

$$P_2 = f_2 (T_1) + C_p M_e \frac{\Delta T}{\Delta t} \quad , \tag{3}$$

where C_p is the specific heat, M_e is mass per unit length of the wire, and $\frac{\Delta T}{\Delta t}$ is the rate of rise of temperature with time. The effect of temperature on radiation losses may be neglected, provided the rate of increase of temperature with time is measured at the instant of the initial increase in temperature; i.e., as $\Delta t \rightarrow 0$,

$$P_2 = f_1 (T_1) + C_p M_e \frac{dT}{dt} \quad ; \tag{4}$$

and

$$P_2 - P_1 = C_p M_e \frac{dT}{dt} \quad . \tag{5}$$

Since the density is also unchanged at the instant the temperature starts to increase,

$$C_p \propto \frac{P_2 - P_1}{\frac{dT}{dt}} \propto \frac{R(I_2^2 - I_1^2)}{\frac{dT}{dt}} \quad , \tag{6}$$

where R is the resistivity of rhenium at the temperature T_1, I_1 is the current through the wire before the step increase in current, and I_2 is the sum of I_1 and the step increase in current.

The apparatus employed for these measurements is illustrated by the sketch in Figure 9. The rhenium was heated to a selected temperature by adjusting the conduction current with the resistor, R_1. A step increase in the current was applied by shorting out R_2. The change in temperature was measured by the output current from the photomultiplier tube. This output current was amplified by a cathode-follower circuit, and its output was applied to the d-c amplifier in the oscilloscope. The sweep time of the

oscilloscope trace was sufficient to allow the wire to attain the higher, stable temperature, T_2. The time for one sweep of the trace on the oscilloscope was approximately 4-1/2 seconds, and was the same for all measurements. The value of the resistance R_2 was adjusted to obtain a temperature difference between T_2 and T_1 such that T_2 is stabilized before the end of the trace. The stable temperatures, T_1 and T_2, were measured with an optical pyrometer. The relationship between brightness and true temperature of rhenium in the temperature range from 1000 to 2600 C is

$$t_t = 1.24\, t_b - 207 \ , \qquad (7)$$

where t_t is the true temperature, C, and t_b is the brightness temperature, in degrees centigrade. This relationship is taken from data determined previously[1].

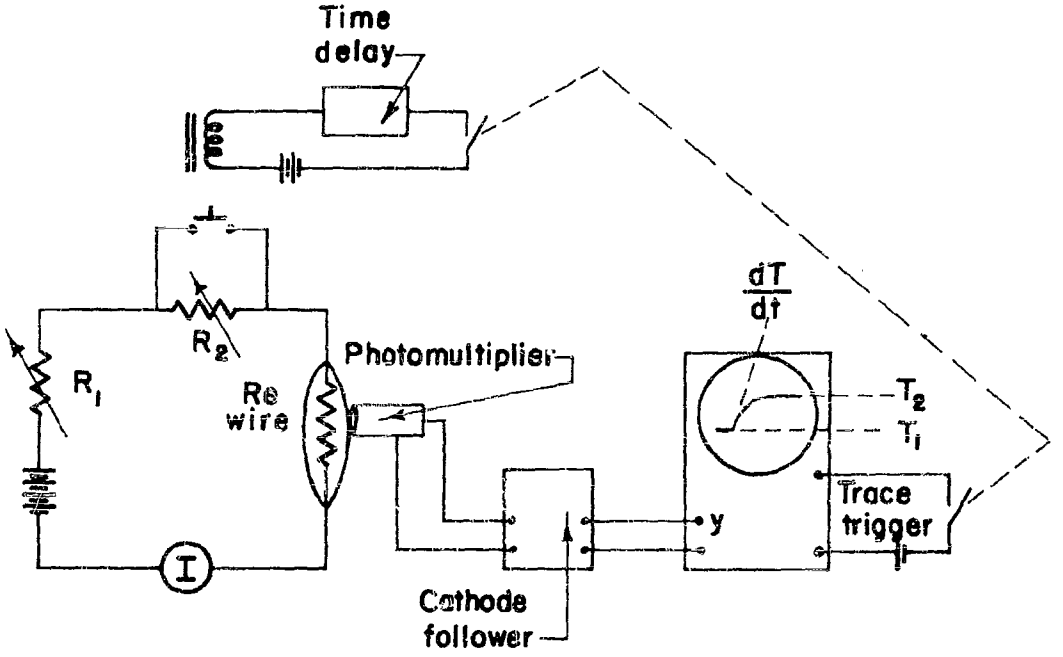

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FIGURE 9. DIAGRAM OF EQUIPMENT FOR SPECIFIC-HEAT MEASUREMENTS

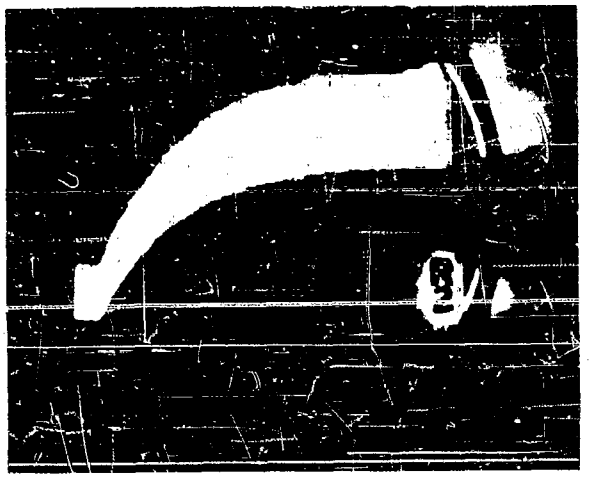
All oscilloscope traces of the change in temperature with time were photographed, enlarged, and printed in order to obtain accurate measurements on the prints. The current was increased stepwise three times at each temperature, and each stepwise increase in the conduction current was

photographed. A typical photograph is presented in Figure 10. The vertical width of the trace is an indication of the pickup of the stray fields in the various circuits. The presence of these fields does not affect the accuracy of the measurements, however, so shielding was not applied to reduce the stray fields to the small value that is required for a narrow trace. From T_1 and T_2 and the time scale of the oscilloscope trace, the initial value of $\frac{dT}{dt}$ was determined. The stepwise variation of the conduction current through the rhenium wire as a function of time is presented in Figure 11.

After measurements on all of the photographs and after reduction of the data, the relative values of the specific heats at different temperatures were those given in Figure 12. Since there are three measurements for each temperature, the vertical lines are drawn to show the range of the probable values, which was calculated from the three measurements at each temperature. The spread in the data is greater than the probable error, but the points show a very definite trend. The temperature range of the measurements is from 1620 to 2690 K and is to be compared with the measurements of Jaeger and Rosenbohm, for which the highest temperature is 1473 K. The line is drawn to obtain the best correspondence between the data from this work and the previously published measurements of Jaeger and Rosenbohm.

The largest error in the measurements arises from the inaccuracy of the measurements of current. It is most unfortunate that a carbon resistor was employed for the permanent current-varying resistor, R_1, in the current-pulsing circuit. Carbon resistors are notorious for variation in resistance under pulse operation. Repeated measurements of the pulse current under presumably constant conditions of operation have shown that the current peak varies from pulse to pulse. Although the average current from two or more pulses was employed in the calculations, the uncertainty in the value of the current is believed to be the largest variable and to account for most of the variations between readings. An error in the current is particularly serious, since the square of the current is employed in the calculations of C_p from $\frac{dT}{dt}$.

For the purposes of comparison, the published values of the specific heat of rhenium and of tungsten are presented in Figure 13. The specific heats for tungsten are from Smithells(17) and the specific heats for rhenium up to 1473 K are from the work of Jaeger and Rosenbohm(4). The dotted line that extends the data of Jaeger and Rosenbohm to higher temperatures is the line from Figure 12, i.e., the experimental curve from these data. Since, on the temperature scale, the measurements from this study do not overlap those from the published work, a basis for extrapolation of the curve was necessary. It was assumed that the magnitude of the specific heat and



Photograph of Response of Rhenium Wire to Rise in Temperature From 2780 to 2900 F

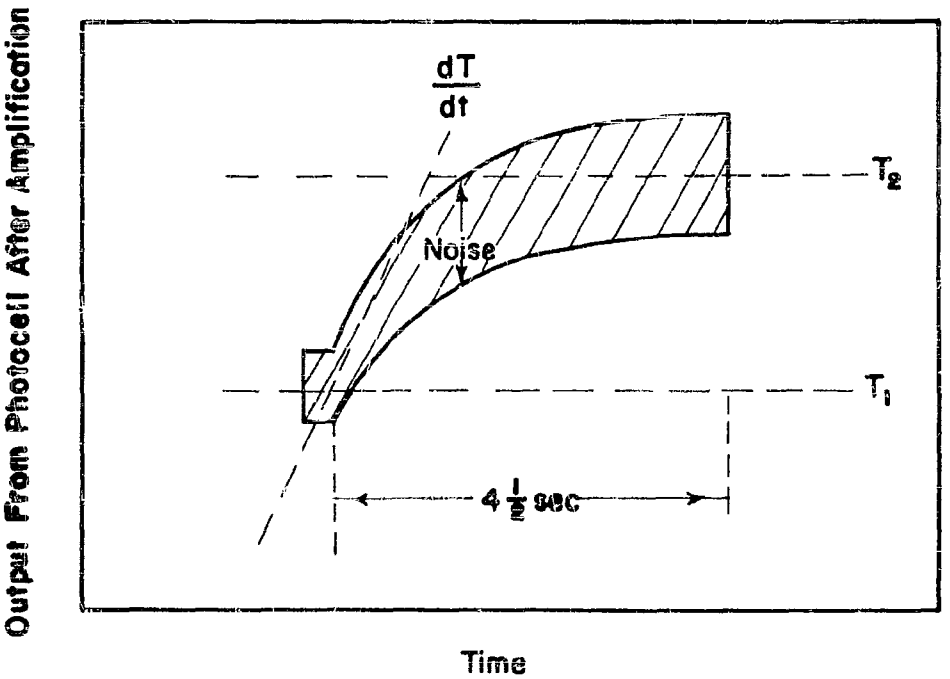
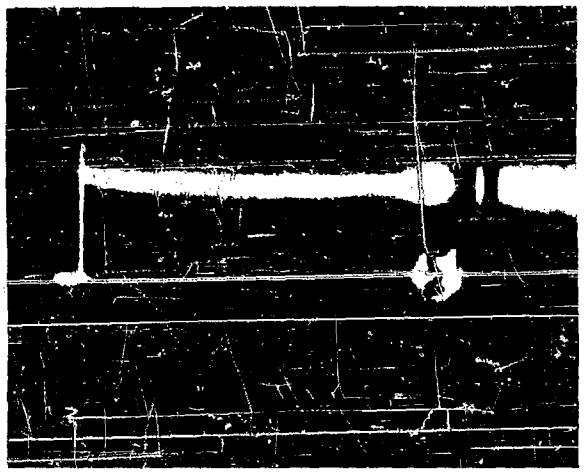


FIGURE 10. A REPRESENTATIVE RESPONSE OF THE SPECIFIC-HEAT APPARATUS TO A STEP INCREASE IN CURRENT



Photograph of Typical Time-Current Relationship

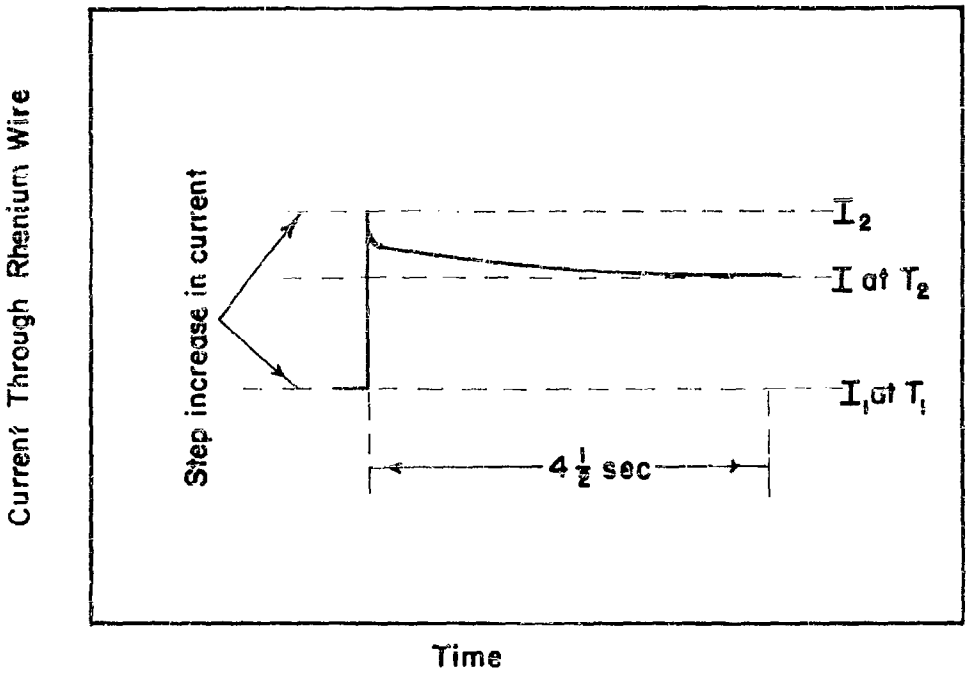


FIGURE 11. RELATIONSHIP BETWEEN CURRENT THROUGH RHENIUM WIRE AND TIME, SHOWING A TYPICAL STEP INCREASE OF THE CURRENT

A-12949

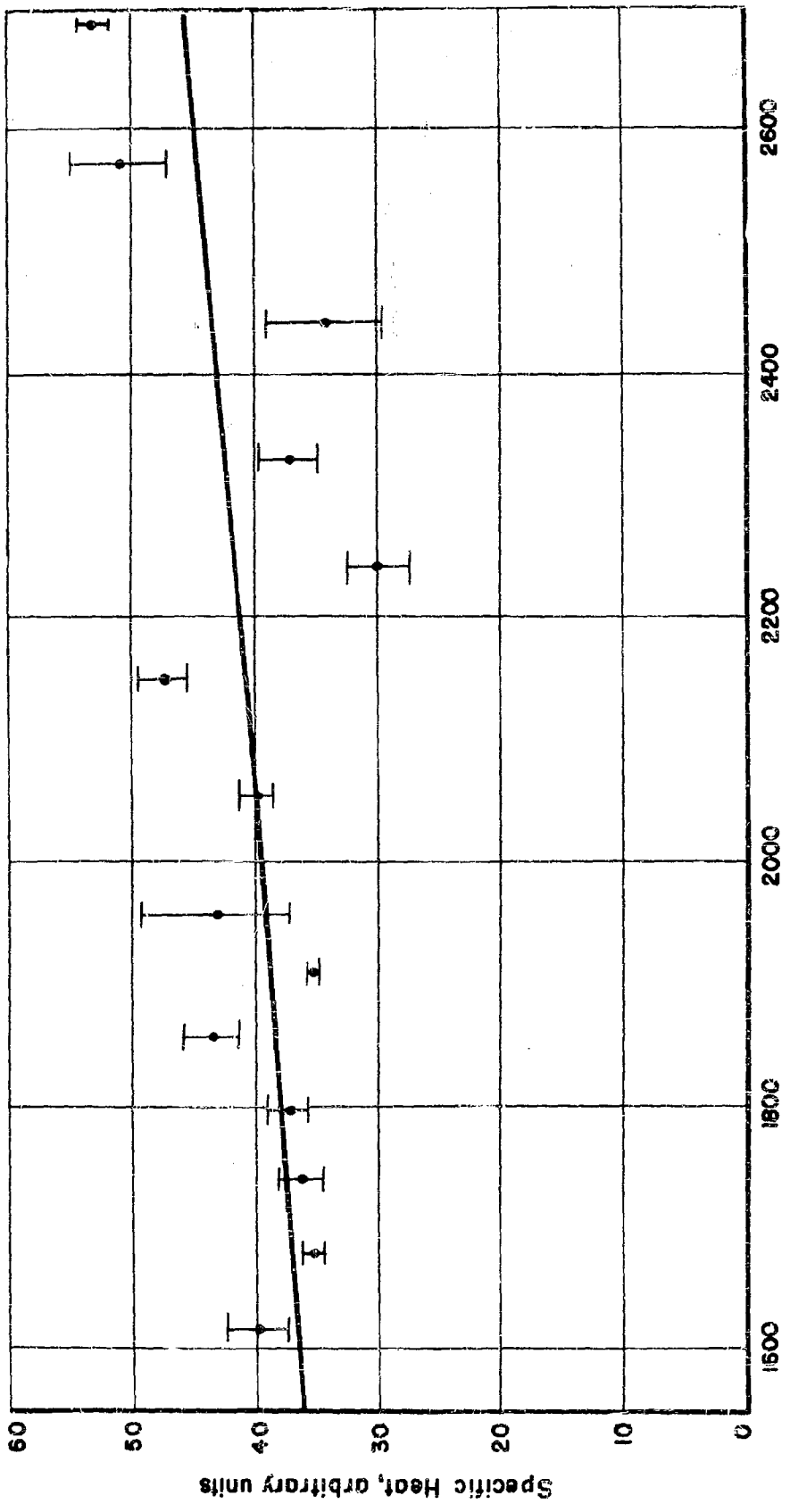


FIGURE 12. SPECIFIC HEAT OF RHENIUM AT HIGH TEMPERATURES

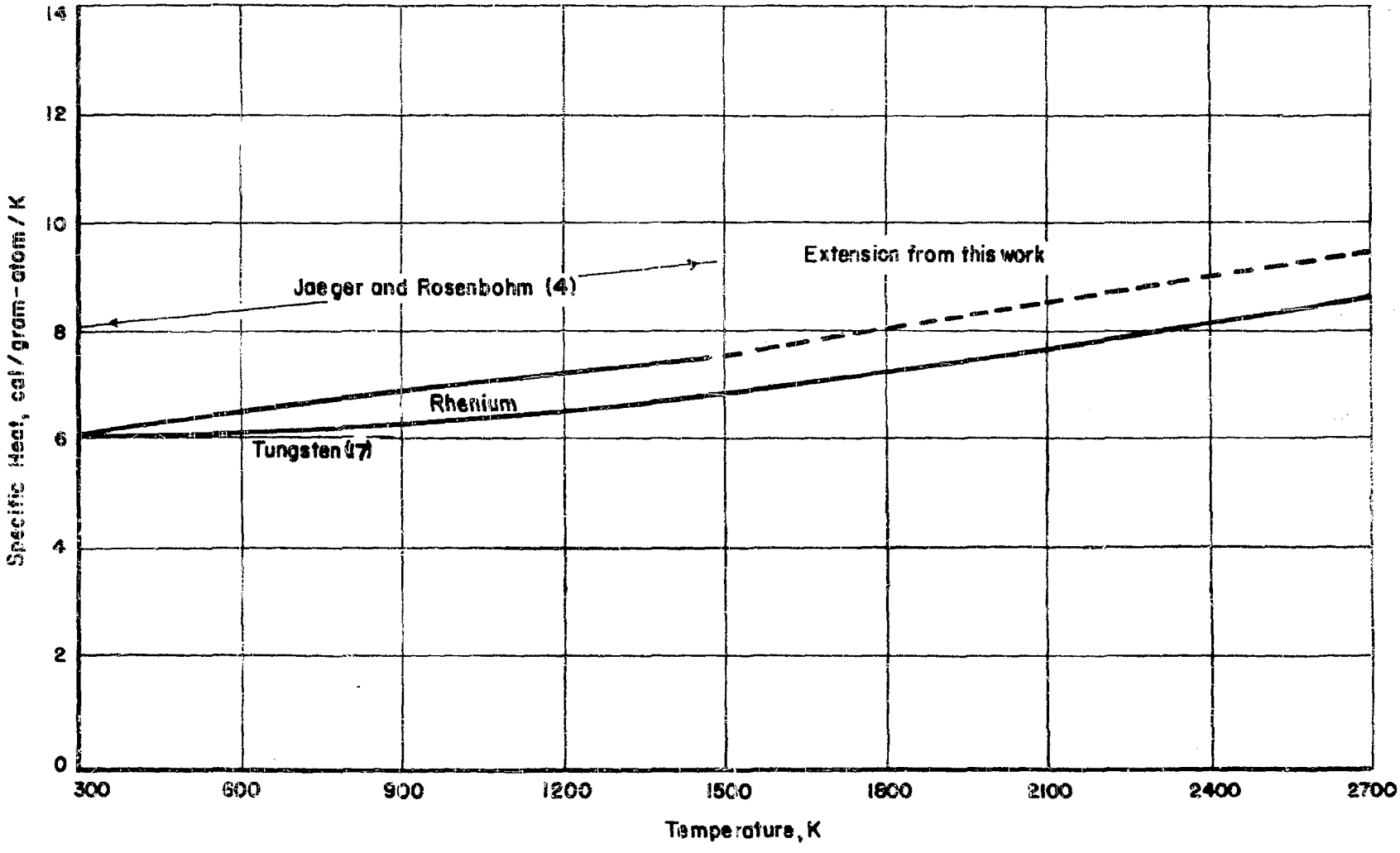


FIGURE 13. COMPARISON OF SPECIFIC HEATS OF RHENIUM AND TUNGSTEN

the slope of the curve of specific heat versus temperature were known at 1473 K (the solid line). The relative magnitude of the values of specific heat from these measurements was then adjusted until the best smooth curve could be drawn through all of the data. The selected curve from these measurements is shown on a large scale in Figure 12, and the relation of the extension to the published data is indicated by the dotted line in Figure 14. The increase in specific heat in this temperature range is attributed to the contribution from electrons. It is also "worth noting that the high-temperature values of the electronic specific heat for tungsten... [is] in agreement with the values calculated from the theoretical energy-level systems".(3) The energy-level systems for rhenium are not so well known as for tungsten, so that calculations are not feasible. From the closeness of these metals in the atomic table, the contributions of electronic specific heats to total specific heat should increase similarly at high temperatures for the two metals.

Vapor Pressure

The accuracy of previous determinations(1) of the vapor pressure was questioned on the supposition that there was an appreciable temperature gradient in the wire. The temperature gradient of a 55-mil wire was determined at 2200 C and 2550 C and found to be so small as to contribute only an insignificant correction to the vapor pressure of rhenium as previously given.

Electromotive Force Studies

Rhenium, either pure or alloyed, has potentialities as a thermoelement material because of its strength, ductility, and high melting point. No information has been reported in the literature concerning the thermal emf of pure rhenium, although rhenium additions to platinum have been discussed.(6) Accordingly, the thermal emf developed by rhenium against platinum was measured, following which measurements were made of the thermal emf generated by Re-Mo, Re-W, and Re-Ta thermocouples. Platinum-base alloys with one and two per cent rhenium vs platinum were also evaluated.

Rhenium vs Platinum

A 20-mil rhenium wire was welded to a 20-mil platinum wire to form a thermocouple 18 inches long. The test couple was surrounded by three Pt-Pt10Rh couples, and the bundle of four couples inserted in a 1/2-inch-diameter closed-end protection tube in a molybdenum-wound tube furnace.

While protected by very slowly moving argon, readings from the three Pt-Pt10Rh measuring couples and the Pt-Re couple were taken. A Leeds and Northrup semiprecision potentiometer was used for recording the emf produced.

Readings were taken from 20 to about 1600 C under the protection of argon. This same general method was also used in taking a second set of data, but in the latter instance the atmosphere was hydrogen. Data obtained were in excellent agreement with the previous measurements under argon. The three Pt-Pt10Rh values were averaged and used to establish the temperature for which the Pt-Re value applied.

The emf-versus-temperature data for the platinum-rhenium couple were plotted and appear to follow the power-series type of equation,

$$E = 1.56 - 0.90 \times 10^{-2} T + 1.29 \times 10^{-5} T^2 ,$$

where E is measured in millivolts and T is in degrees Kelvin. In Figure 14, the plot of this equation is compared with the experimental data.

The first derivative of the thermal emf equation gives the thermoelectric power, $P = -9.0 + 2.58 \times 10^{-2} T$, microvolts per degree. The thermoelectric power of rhenium increases linearly with increasing temperature. Thus, the Re-Pt couple has increasing sensitivity with increasing temperature; as a thermocouple element, rhenium should be most useful at high temperatures.

Figure 15 shows the emf produced by rhenium and other metals with reference to platinum. The figure shows that the W-Mo couple, which has been used in industry for many years, produces an emf of about 2 mv at 1600 C and only about 7 mv at 2200 C[7]. It is apparent that the Re-Mo or Re-W thermocouples would be expected to produce an emf of about 30 mv at 1600 C. Thus Re-Mo and Re-W thermocouples might be of value for high-temperature measurement because of the high emf's apparently possible. The promise of Re-W and Re-Mo thermocouples, as indicated in Figure 15, resulted in the studies of these and the Re-Ta thermocouple which follow.

Rhenium vs Tungsten, Molybdenum and Tantalum

Re-W, Re-Mo, and Re-Ta thermocouples were prepared by helium-atmosphere welding of beads on 20-mil wires of the component metals. The temperature-vs-emf relationships of these couples were measured under a vacuum of 0.4 to 4.0 microns by putting the thermocouple beads into a cavity in a large self-resistance-heated molybdenum rod. Temperature of

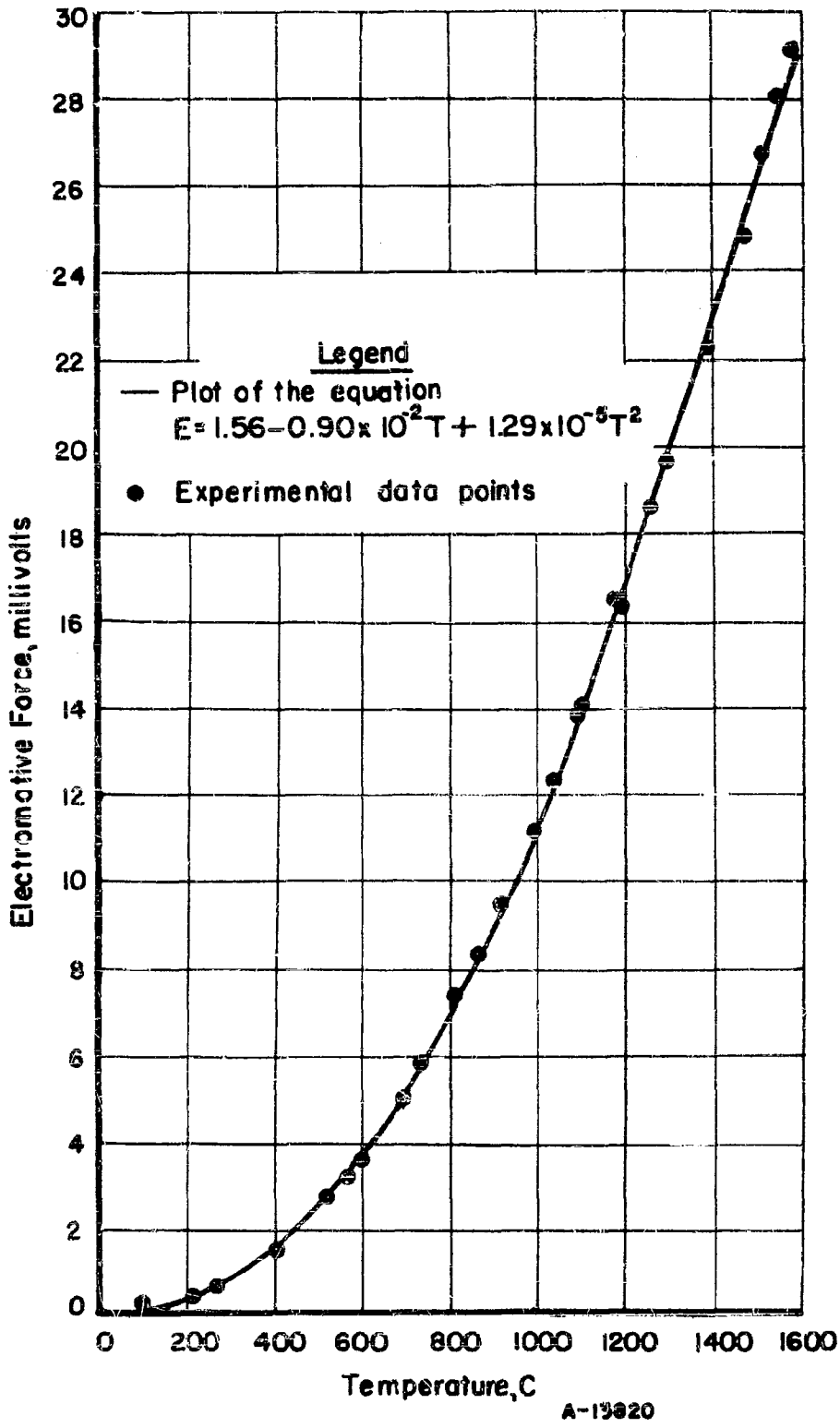


FIGURE 14. EXPERIMENTAL POINTS AND CALCULATED CURVE OF THE THERMOELECTRIC FORCE PRODUCED IN A PLATINUM-RHENIUM THERMOCOUPLE

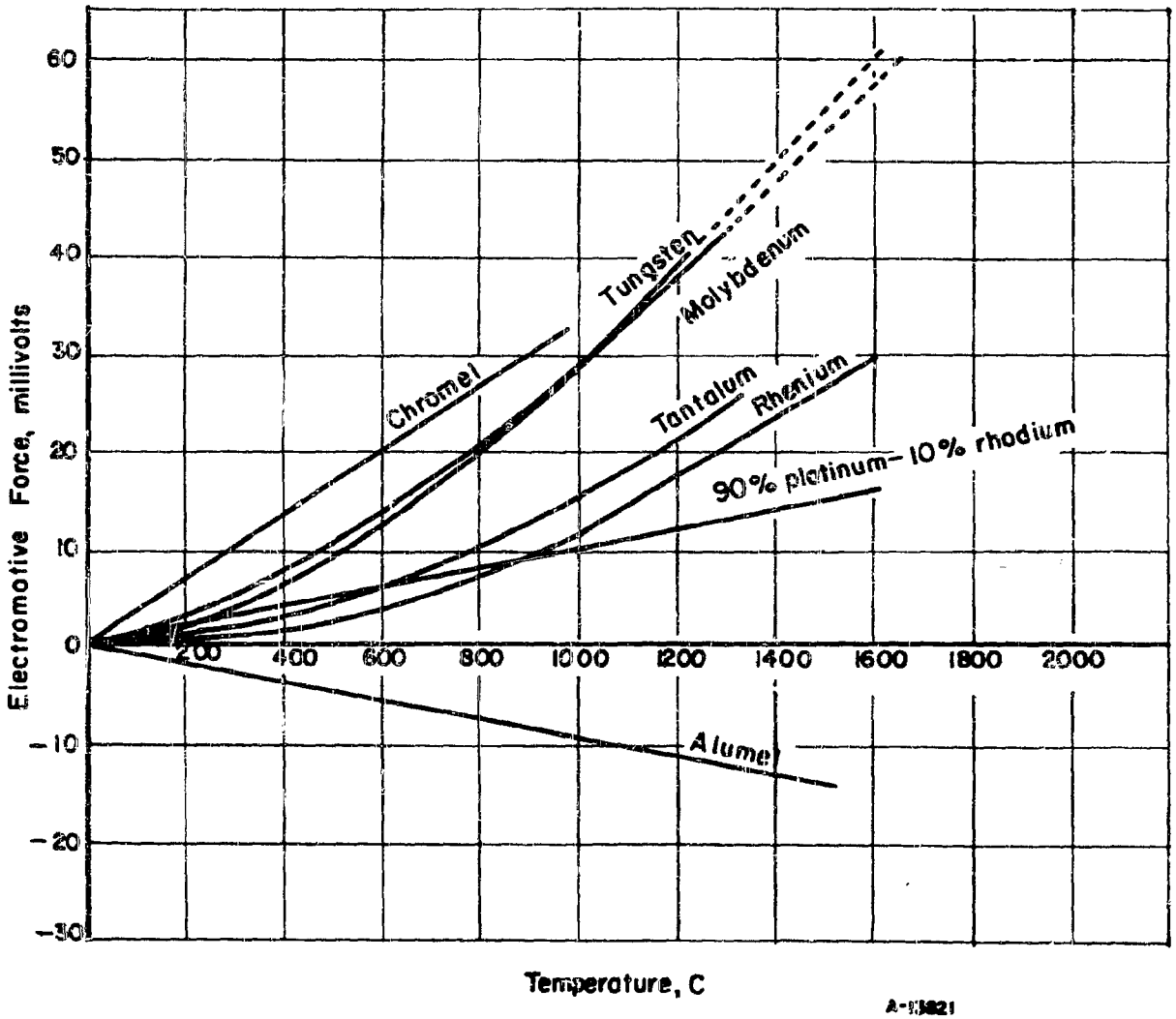


FIGURE 15. ELECTROMOTIVE FORCE VERSUS TEMPERATURE FOR CERTAIN METALS WITH RESPECT TO PLATINUM

The data for this graph were taken from several sources. The Chromel, Alumel, and 90 Pt-10 Rh curves are as reported by Wood and Cork[8]. The tantalum, tungsten, and molybdenum curves up to 1200 C are reproduced from data in The International Critical Tables[9]. Tungsten and molybdenum couples produce an emf of about 2 mv at 1000 C[7]. Therefore their curves have been extrapolated to show this effect and provide a better visual comparison with rhenium.

the molybdenum rod was measured optically by means of a black-body hole. The thermal emf's generated by the three thermocouples over the temperature range from 800 to 2500 C were recorded on a semiprecision potentiometer. The experimental data is shown in Figure 16.

The thermal emf's generated by the Re-W and Re-Mo couples are as estimated from the Re-Pt data using published values for the Pt-W and Pt-Mo couples. Both the Re-W and Re-Mo couples produce high emf's, with good sensitivity to temperature, though the emf's are not quite as high as estimated from the earlier Re-Pt work. The Re-Ta couple produced an emf with insufficient potential to be of practical use.

Attempts to fit parabolic or hyperbolic equations to the molybdenum and tungsten curves were unsuccessful, particularly because of the linearity of the Mo-Re data above 1700 C, and of the W-Re data in the ranges from 800 to 1700 C and from 1700 C to 2500 C. Accordingly, linear equations were developed for the straight-line portions of the data, and a parabolic equation for half of the molybdenum data as follows:

Molybdenum vs Rhenium	800-1700 C	$E = 25.8 - \frac{18,400}{T}$
	1700-2500 C	$E - 0.00485T + 7.6$
Tungsten vs Rhenium	800-1700 C	$E = 0.0151T - 9.8$
	1700-2500 C	$E = 0.00957T + 1.3$

In these equations, E is the electrometric force in millivolts and T the absolute temperature in degrees Kelvin. The equations are plotted with the raw data in Figure 16. The first derivative of these equations gives the thermoelectric power, P, such that

$P = \frac{dE}{dT} \times 10^3$, the thermoelectric power in microvolts per degree.

Molybdenum	800-1700 C	$P = \frac{18.4}{T^2} \times 10^6$
	1700-2500 C	$P = 4.85$
Tungsten	800-1700 C	$P = 15.1$
	1700-2500 C	$P = 9.57$

As shown by the thermoelectric power and by the slope of the curves in Figure 16, the Re-W thermocouple produced a greater change in emf with temperature (thermoelectric power or "sensitivity") than did the Mo-Re couple, and a greater total emf at temperatures above 1500 C. In addition, the Re-W thermocouples are potentially useful at temperatures up to about 2800 C, the eutectic temperature in the system. Re-Mo thermocouples are

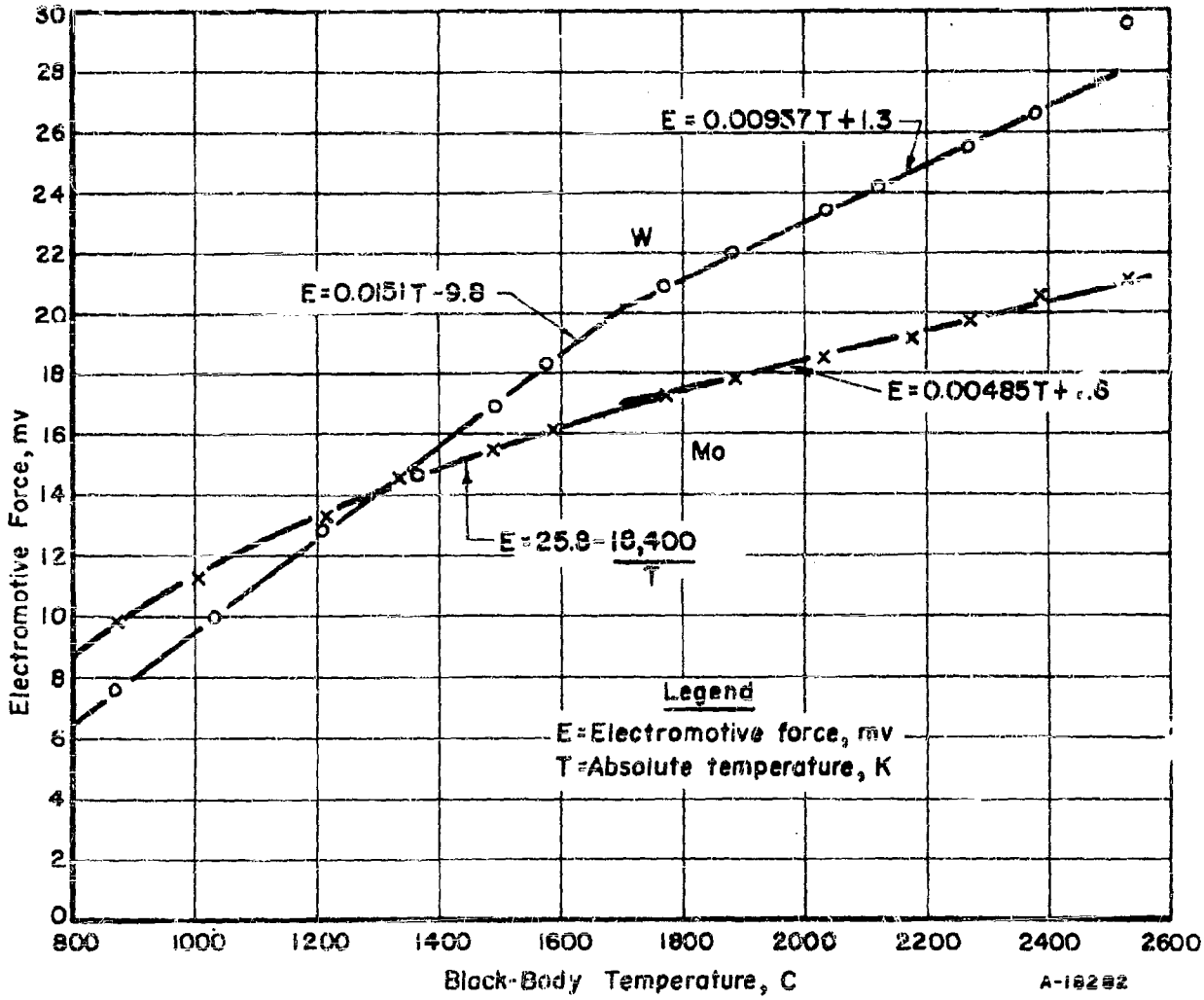


FIGURE 16. EXPERIMENTAL DATA AND MATCHING CURVES CALCULATED FOR THE THERMAL ELECTROMOTIVE FORCE PRODUCED BY RHENIUM-MOLYBDENUM AND RHENIUM-TUNGSTEN THERMOCOUPLES

of interest up to about 2500 C. However, both tungsten and molybdenum in thermocouples will be subject to brittleness from recrystallization following exposure to high temperatures, while the rhenium would be expected to remain ductile. Any thermocouples containing tungsten, molybdenum, or rhenium would, of course, be useful only in a neutral or reducing atmosphere, so that the deleterious oxides of these metals would not form and destroy the couples.

MECHANICAL PROPERTIES

The previous technical report[1] included the results of a number of mechanical properties determinations on rhenium. Most of the properties reported were found for rhenium rod or rhenium wire. In the more recent work, additional mechanical properties have been studied on rod and wire and also on sheet and foil, so that a more complete picture of the mechanical property behavior of rhenium can be drawn.

Tensile Properties of Cold-Rolled Sheet

Ten-mil rhenium strip was cold rolled from sintered bar, and a section removed for tensile testing. The remaining strip was reduced in 10 per cent stages and sections were removed until about 30 per cent total reduction was reached. Tensile and hardness data were obtained for each reduction step.

Tensile specimens prepared from the strip were all standard-type tensile specimens with an 0.2-inch reduced-section width and a 1-inch gage length. Initial strain was measured by means of Type A-7 strain gages. Dividers were used to record extensions beyond the limit of the strain gages. Strain rate was 0.01 inches per minute.

The tensile data are presented in Table 5, while the ultimate tensile strength, 0.2 per cent offset yield strength, and elongation are reported in graphical form in Figure 17 as a function of cold work. The offset yield strength and ultimate tensile-strength curves show a marked increase in strength with increase in cold work, as observed previously for cold-worked wire[1]. The total elongation of annealed sheet was found to be 28 per cent. This is the highest value found yet for rhenium, since annealed rod was found to have an elongation of about 25 per cent, and an annealed wire had about 10 per cent[1]. At 20 to 30 per cent reduction, the elongation drops to 2 per cent because of severe work-hardening.

TABLE 5. TENSILE AND ELONGATION DATA FOR ANNEALED AND COLD-ROLLED RHENIUM SHEET

Standard-type, 0.2-inch reduced section, 1-inch gage length

	Annealed	Reduced 12.9 Per Cent	Reduced 24.7 Per Cent	Reduced 30.7 Per Cent
Rolled Thickness, mils	10.1	8.8	7.6	7.0
Proportional Limit, psi	31,700	25,200	42,200	159,000
0.1 Per Cent Offset Yield Strength, psi	131,000	233,000	279,000	282,000
0.2 Per Cent Offset Yield Strength, psi	135,000	245,000	298,000	311,000
Ultimate Tensile Strength, psi	168,000	250,000	307,000	322,000
Elongation in 1 Inch, per cent	28	8	2	2
Reduction of Area, per cent	30	24	1	1

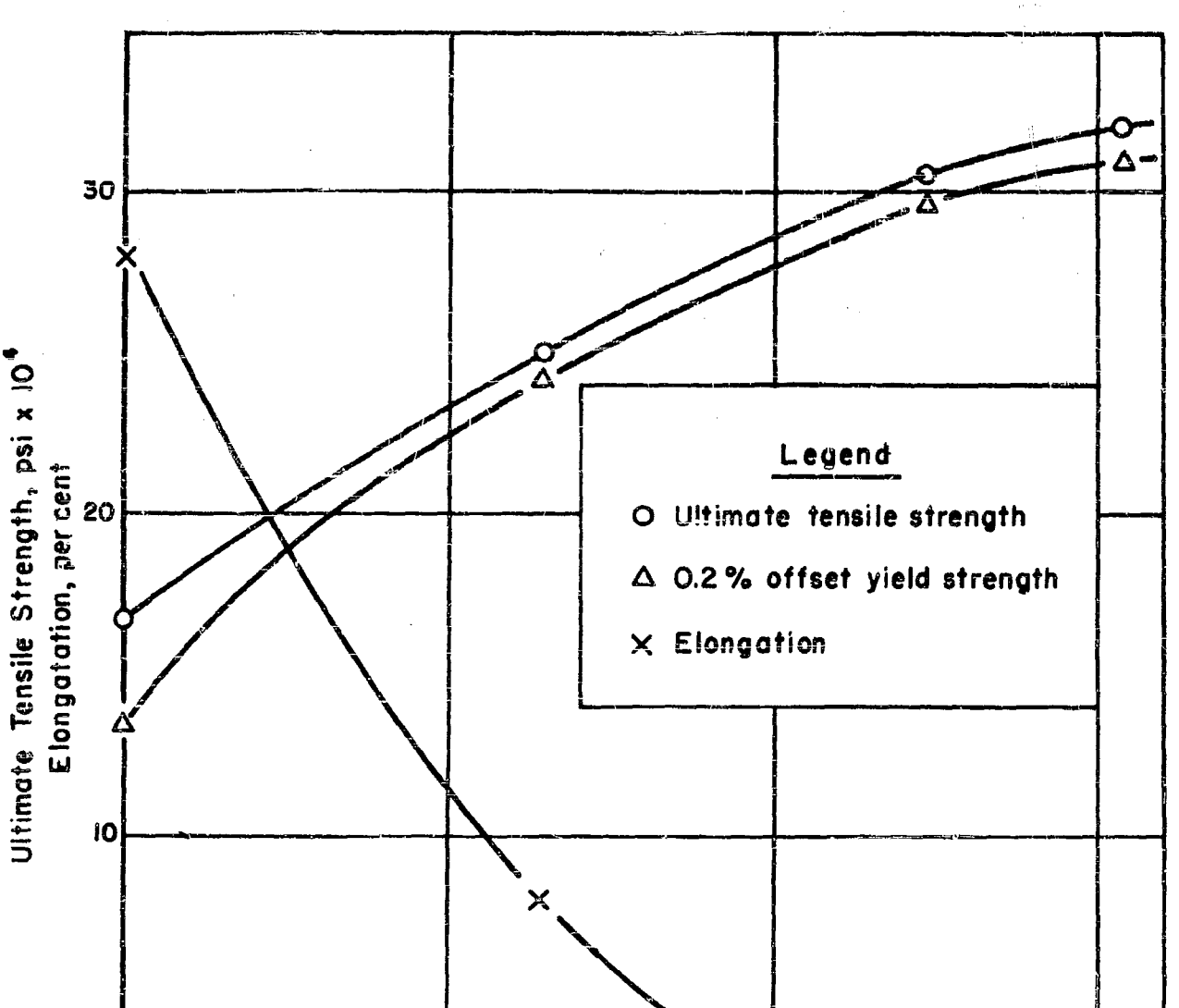


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FIGURE 17. TENSILE PROPERTIES OF ANNEALED AND OF COLD-ROLLED RHENIUM SHEET

Work-Hardening Characteristics of Rod, Sheet, and Wire

The high work-hardening rate of swaged rhenium rod has been reported previously(1). Hardness values of over 800 VHN have been attained with 30 per cent reduction in cross-sectional area from rod with an annealed hardness of about 270 VHN. Further work-hardening studies were subsequently conducted on drawn wire, rolled sheet, and rolled arc-melted metal.

The 10-mil cold-rolled strip discussed above was used for some of these work-hardening studies. The surface hardness and cross-section hardness were determined at the various reduction steps; little difference was noted between the hardness values measured in the two directions. Another series of hardness measurements was made on a 3/4-inch-diameter 30-gram arc-melted button, cold rolled to a 0.15-inch thickness. After annealing, various further reductions, up to 40 per cent, were taken by cold rolling, and hardness values were recorded. Wire 60 mils in diameter was reduced by wire drawing about 20 per cent in cross-sectional area, then an additional 20 per cent by swaging with intermediate hardness measurements being taken.

Figure 18 shows the work-hardening characteristics of the several types of fabricated rhenium compared with those of nickel. All of the rhenium specimens exhibit a high degree of work-hardening except the rolled 10-mil sheet, which work-hardened only relatively slightly. It is noteworthy that this material had by far the smallest dimension (7 to 10 mils) separating the surfaces being worked. This dimension probably was sufficiently large, however, not to interfere with movement of the metal grains, which were about 0.01 mm in diameter (0.4 mil). As shown by Figure 18, both the cross-sectional area of the specimen and the method of working affect the work-hardening rate; large sections and rounds promote higher rates.

Shear Modulus of Elasticity

The shear modulus of rhenium (the modulus of rigidity) was determined at room temperature on a 50-mil wire containing 0.75 per cent thorium (as ThO_2) by means of a torsional pendulum. The value was found to be 22.6×10^6 psi. In addition, Poisson's ratio was calculated to be 0.49, using the Young's modulus value of 67.5×10^6 psi previously reported. However, calculation of Poisson's ratio from these data is very sensitive, and a 1 per cent error in either the shear modulus or Young's modulus will produce about a 10 per cent error in Poisson's ratio. Since the calculated Poisson's ratio was very high, experimental determination of the value might be of interest.

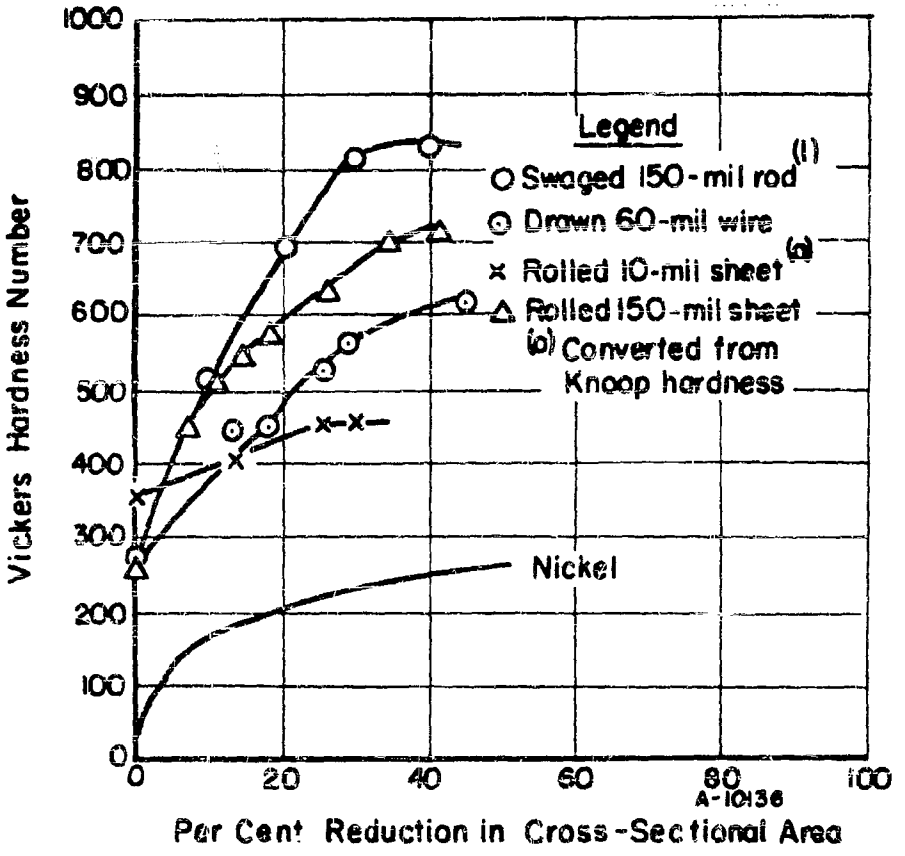

FIGURE 18. COLD WORK-HARDENING CHARACTERISTICS FOR VARIOUS TYPES OF RHENIUM COMPARED WITH THOSE OF NICKEL

Modulus of Elasticity Variation With Temperature

A 1/8-inch-diameter annealed rhenium rod, 6 inches long, was used to determine Young's modulus from room temperature to 880 C (1620 F). The rod was activated in a transverse-vibration apparatus suspended in a helium atmosphere furnace. The drive frequencies of the rod were varied until resonance occurred and the modulus values calculated. The driven frequency at resonance was 569 cycles per second. The data, plotted in Figure 19, show that the modulus decreases with temperature in an approximately linear manner over the range tested.

Stress-Rupture Properties

50-mil high-purity rhenium wires were resistance heated to various temperatures while loaded in tension and the rupture times recorded. A protective helium atmosphere containing 2 to 5 per cent hydrogen was used, and the temperature was measured by optical means.

A preliminary series of rupture tests was conducted at 1000 C. As shown in Table 5, the rupture time was 16.5 hours at a stress of 40,000 psi. These data were related to the short-time tensile data previously reported[1] by a tentative Larsen-Miller-type plot[11] from which the breaking stresses for 20-hour rupture tests at other temperatures were estimated. Tests were then run at the various elevated temperatures, using the stresses recorded in Table 6, which reports the rupture time and ductility data found. These stress-rupture data were then related to the short-time elevated-temperature tensile data determined previously as shown in Figure 20. The best value of K was found to be 5. Figure 20 also includes scales which relate stress to temperature for rupture times of 100 and 1000 hours.

The hot-short behavior previously found for rhenium during attempted hot fabrication in air does not cause extreme brittleness under stress-rupture conditions in a neutral atmosphere, although elongation drops to a value of about 1 to 3 per cent above 500 C. Unlike the short-time tensile characteristics, elongation in stress-rupture tests was found to increase to over 4 per cent at 2000 C; quite possibly increased ductility would be experienced with further increase in temperature. This improved ductility at very high temperatures is expected. Such behavior usually commences at about the recrystallization temperature with other metals, but seems to occur higher with rhenium.

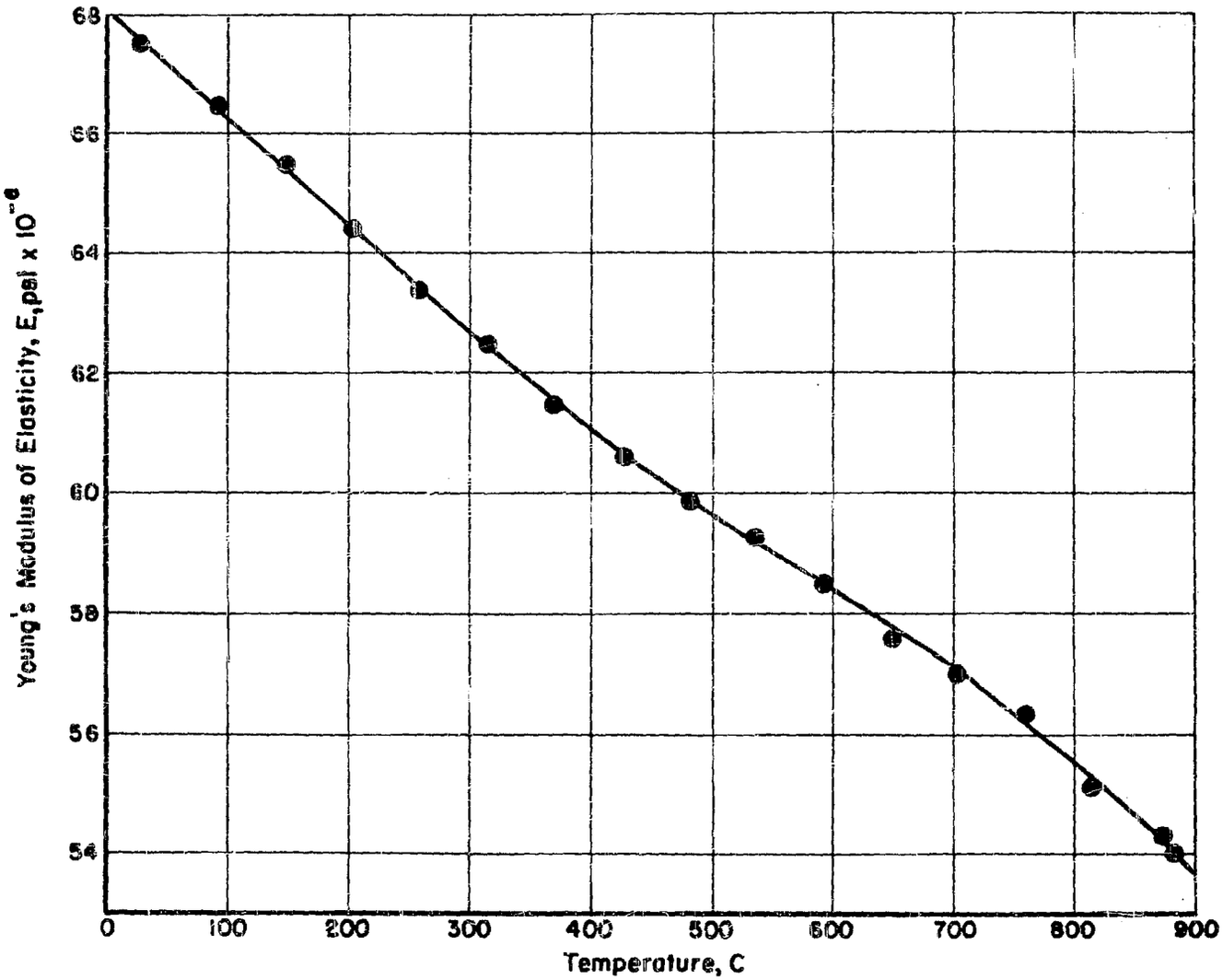

FIGURE 19. VARIATION OF THE MODULUS OF ELASTICITY OF RHENIUM WITH TEMPERATURE

TABLE 6. STRESS-RUPTURE CHARACTERISTICS OF 50-MIL RHENIUM WIRE AT 1000 C

Breaking Stress, psi	Rupture Time	Elongation, per cent
80,000	30 seconds	2 (in 3.1 inches)
70,000	40 seconds	2 (in 3.1 inches)
60,000	5.0 minutes	2 (in 3.1 inches)
50,000	3.7 minutes	2 (in 3.1 inches)
40,000	16.5 hours	2 (in 4.6 inches)

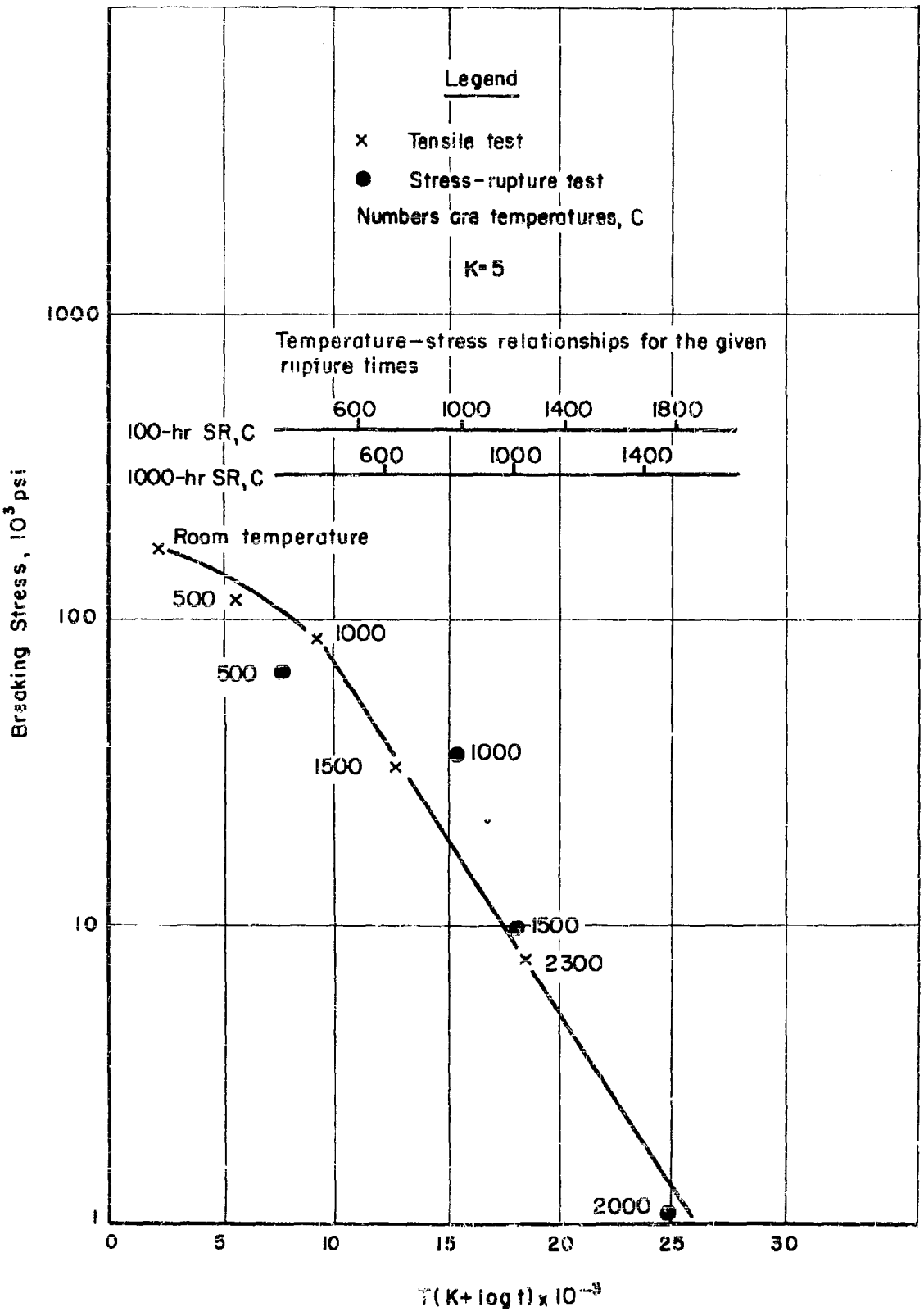

FIGURE 20. PARAMETRIC PLOT OF TENSILE AND RUPTURE DATA FOR PURE RHENIUM METAL

ELECTRONIC PROPERTIES

Thermionic Emission of Thoriated Rhenium

The thermionic emission from a rhenium wire that contained 1 per cent thorium, added as ThO_2, has been reported previously[1]. The emission was several orders of magnitude lower than that of thoriated tungsten at comparable temperatures. In order to determine the possible value of higher thorium contents on rhenium wire, thermionic emission measurements were conducted on a rhenium wire containing 2 per cent thorium, added as ThO_2.

The apparatus employed for these measurements was essentially the same as that employed in the earlier measurements. The diameter of the wire was 0.020 inch. This wire was inserted into the guard-ring diode previously described[1]. The guard-ring diode enclosure was evacuated and sealed off from the pumps after thorough outgassing. The final pressure after seal-off was of the order of 10^{-8} mm of Hg, as indicated by a Sylvania VG-1A manometer.

The rhenium wire was initially heated for a short period at a temperature of approximately 2300 C. Temperature measurements and saturation emission current for a selected temperature were obtained after the selected temperature had been maintained for several hours. The saturation currents were obtained from the Schottky slopes in the plot of the log of the current versus the square root of the field strength. An optical pyrometer was employed for the temperature measurements.

The Schottky slopes for four temperatures are shown in Figure 21. The saturation currents are as follows:

Temperature, K	Saturation Currents, amp/cm^2
1833	1.65×10^{-4}
1894	3.73×10^{-4}
1944	6.09×10^{-4}
2005	8.48×10^{-4}

These values were inserted in a Richardson plot for determination of the equivalent work function (see Figure 22). For the three lowest temperatures the plot is a straight line. However, the value at the highest temperature measured falls off this line. If a straight line is drawn through the values at the three lowest temperatures, an equivalent work function of 2.7 ev is found with a corresponding A value of 0.01 amp/cm^2.

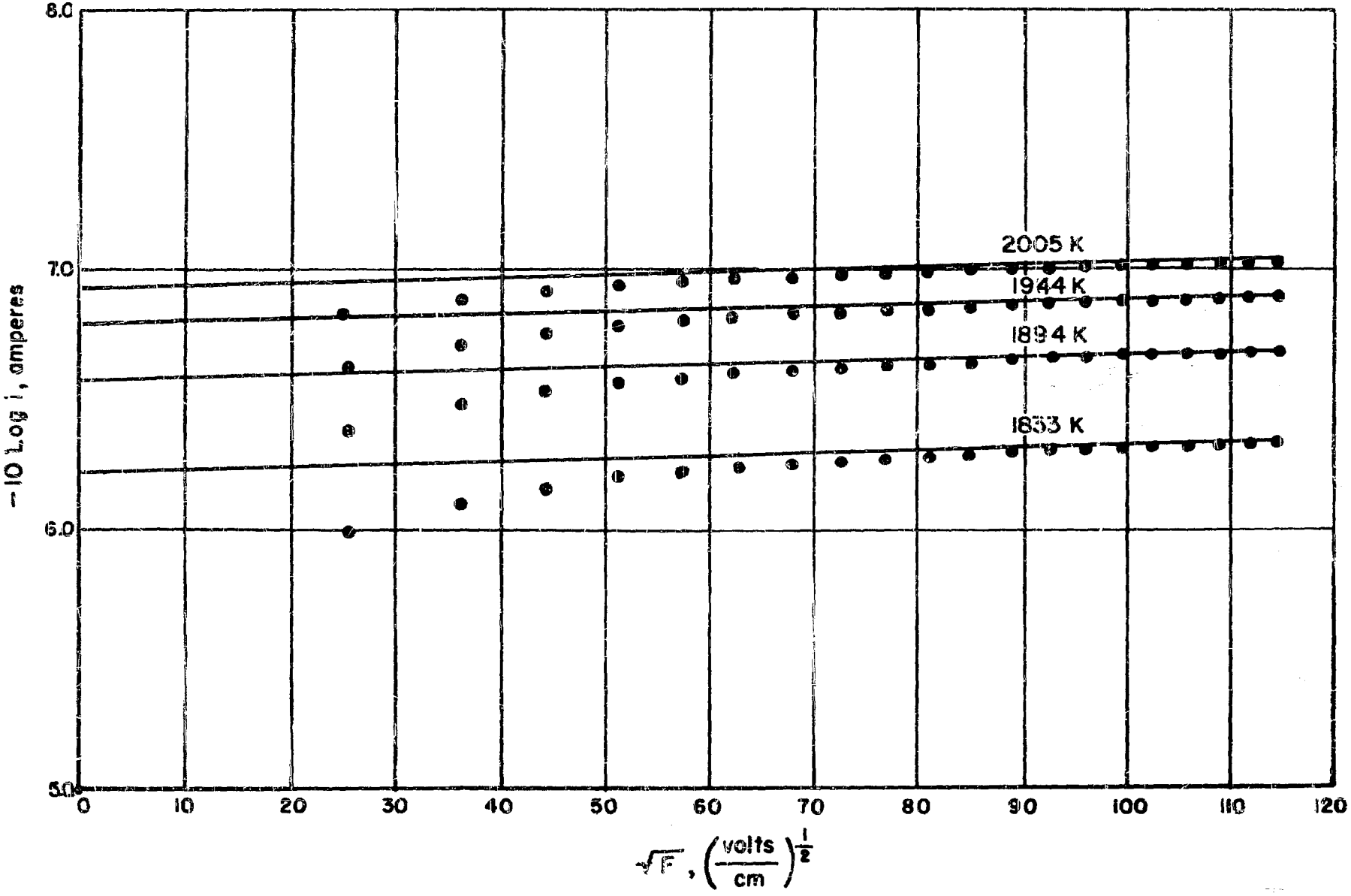

FIGURE 21. SCHOTTKY SLOPES FOR THORIATED RHENIUM WIRE

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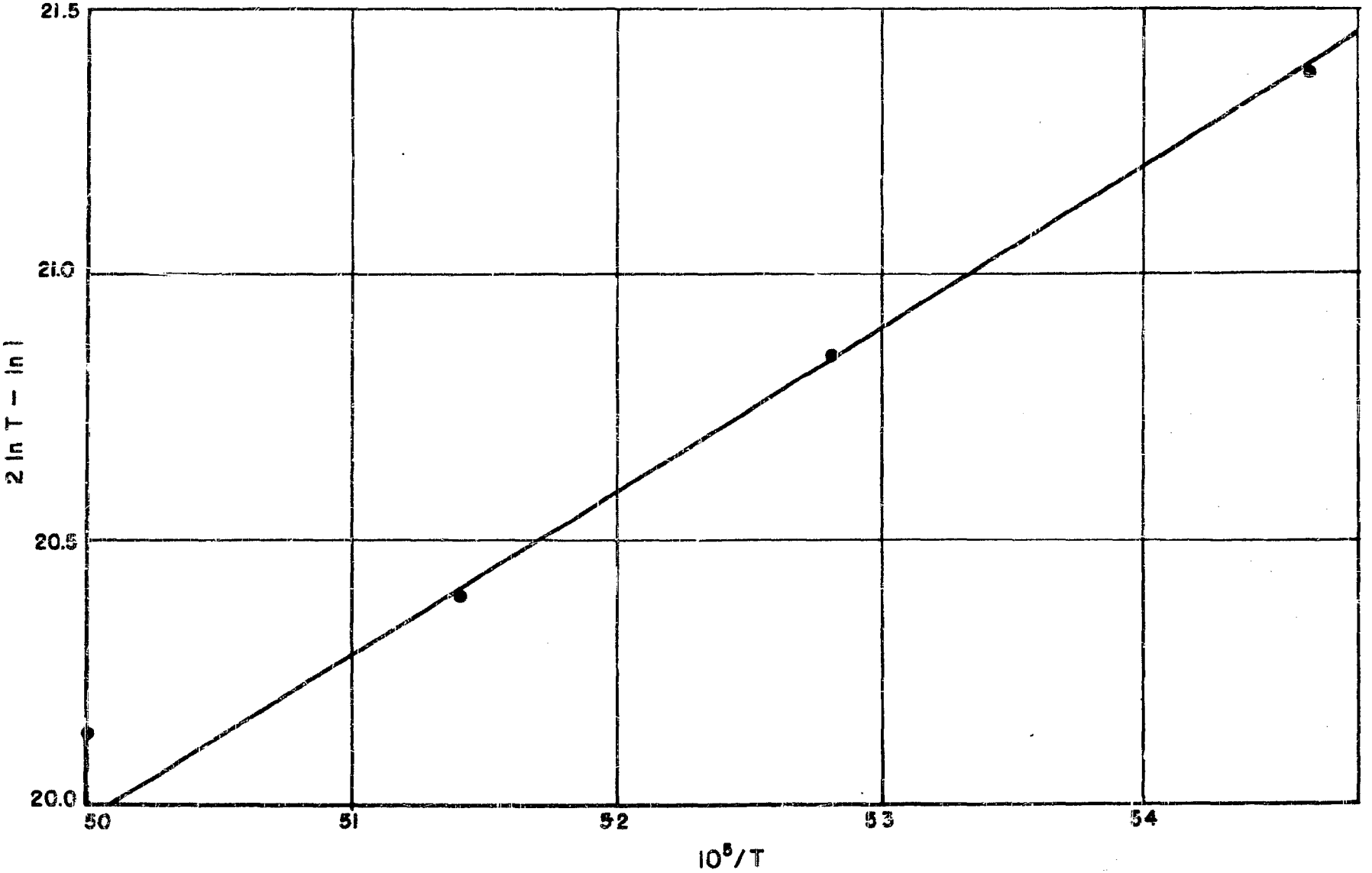

FIGURE 22. RICHARDSON PLOT FOR THORIATED RHENIUM WIRE

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In this very short survey of the properties of thoriated rhenium, several questions were not resolved. If a complete layer of thorium was on the rhenium surface, the expected emission would have been much higher than was obtained here. Obviously, this condition was not met in this measurement, and the diffusion rate of thorium in rhenium needs study. This is only one example of the questions still facing those that work with rhenium.

To take advantage of the properties of rhenium and to satisfy the need for high electron emission, a more thorough study of thoriated rhenium is needed. Some of the points which should be included in such a study are: (1) the diffusion rate of thorium in rhenium as a function of temperature, (2) the evaporation rate of thorium from a rhenium surface as a function of temperature, (3) the resistance to back bombardment of thorium on a rhenium surface, (4) a study of the breakdown of ThO_2 in rhenium, and (5) a study of the mechanical properties of rhenium to which ThO_2 has been added so that an optimum amount of ThO_2 can be found, consistent with good mechanical properties and good thermionic emission.

As has been shown throughout this project, it is expected that rhenium would be a better choice than tungsten in certain electron tube applications, for example, where the presence of water vapor is unavoidable or where getters may not be used.

The Photoelectric Threshold of Rhenium

The determination of the photoelectric work function of rhenium was completed during this report period. Photoelectric measurements on a strip of outgassed rhenium gave a value for the work function of $\phi_0 = 4.66 \pm 0.01$ ev or $\lambda_0 = 2662 \pm 4$ Å when Fowler's method for determination of the threshold was applied to the data.

The only previous work reported on this problem is that of Engelman[12], who reported a probable value of $\phi_0 = 4.98$ volts and $\lambda_0 = 2480$ Å. This value was obtained for rhenium deposited on a tungsten wire.

The thermionic work function was found to be 4.8 ev in earlier work on this project[1]. Because of this and the fact that Engelman had to extrapolate his value of the photoelectric work function, it appeared that a check of Engleman's value would be advisable and the present work was undertaken.

A diagram of the experimental phototube used in the present work is shown in Figure 23. The rhenium, in the form of ribbon 1 x 5 x 0.013 cm, was held by nickel supports and could be heated by passing current through it. "A" has a nickel loop which served as the anode. The shield, "S", had a small rectangular hole in it which allowed the light to hit only the rhenium on the cathode. "Q" was a quartz lens which focused the light on the rhenium.

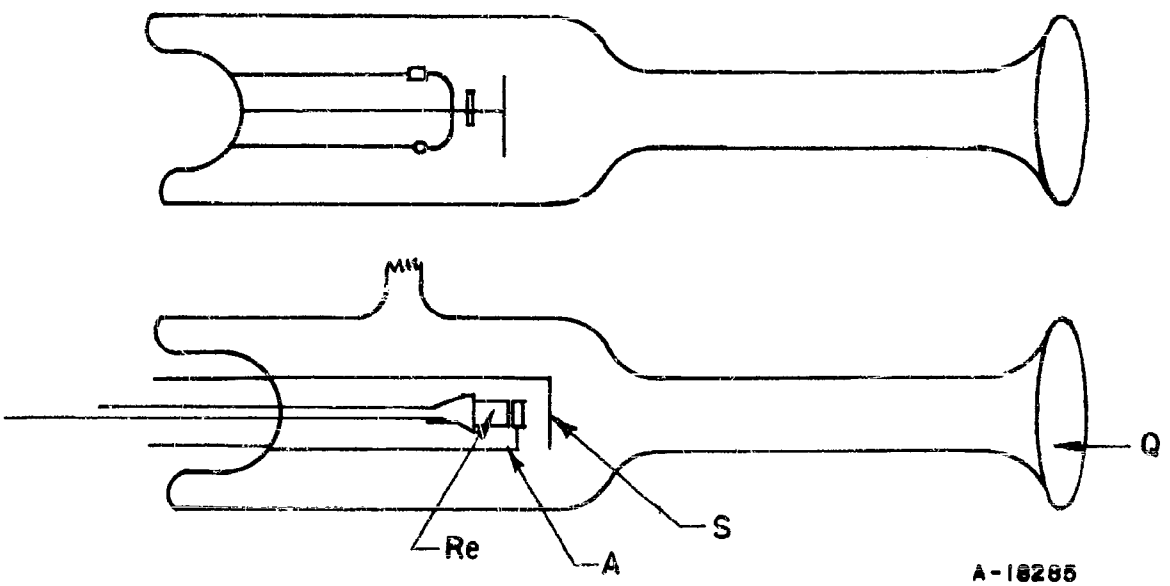

FIGURE 23. EXPERIMENTAL PHOTOTUBE FOR PHOTOELECTRIC-THRESHOLD MEASUREMENTS

All parts of the tube were carefully cleaned before assembly. The glass was cleaned by a conventional glass-cleaning solution, the nickel parts by electropolishing, and the rhenium by hot concentrated hydrochloric acid. The tube was pumped for approximately 240 hours' degassing time. This included 120 hours during which the rhenium was at a temperature of 1000 to 1200 C. For most of the remaining time, the tube was heated in an oven at 450 C. The metal parts and getters were also heated by induction several times during this period. At the end of degassing, the getters were fired and the tube sealed off at a pressure of approximately 2×10^{-7} mm Hg while the rhenium was at approximately 1260 C. After seal-off, the rhenium was heated at 1000 to 1200 C for about 250 hours, so that the total outgassing time on the rhenium included around 220 hours at 1000 C and 150 hours at 1200 C.

To determine the photoelectric work function, a spectral response curve is obtained by measuring the photocurrent per unit light intensity as a function of the wave length of the incident light. A Hilger quartz monochrometer was used to isolate a narrow band of wave lengths. Its slit widths were usually from 0.25 to 0.5 mm. This corresponds to a maximum bandwith in the experimental region of 15 to 30 Å. A diagram of the experimental apparatus is shown in Figure 24.

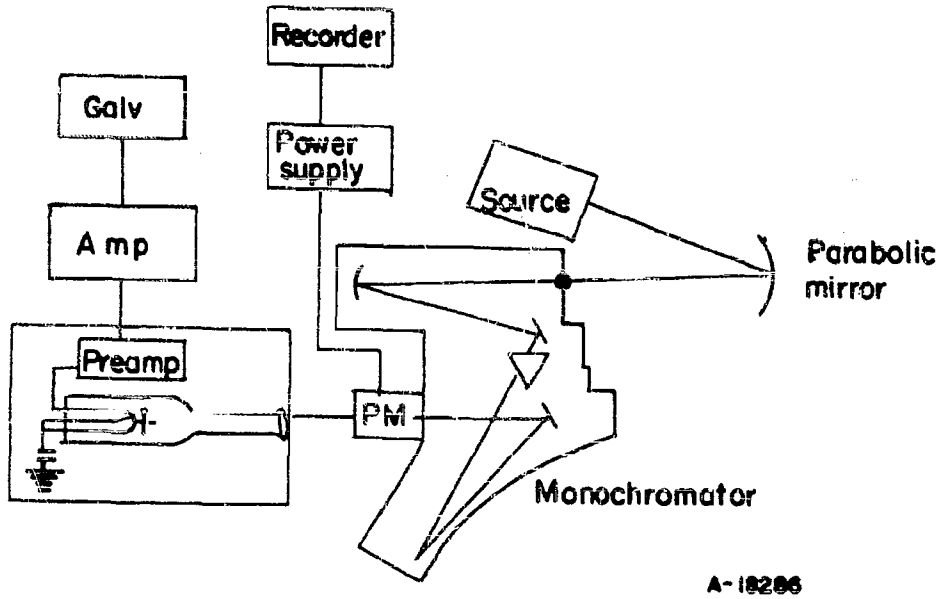

FIGURE 24. DIAGRAMMATICAL REPRESENTATION OF APPARATUS FOR THE DETERMINATION OF PHOTOELECTRIC WORK FUNCTION

In the first attempts, a carbon arc was used as a source of ultraviolet radiation. This did not furnish enough energy in the ultraviolet, so a BHG high-pressure, air-cooled mercury lamp was employed which was kindly loaned to Battelle by Dr. E. E. Bell of The Ohio State University Physics Department. This source, though not completely ideal, emits sufficient energy in the ultraviolet for the purposes of this work. Its spectrum consists of greatly pressure-broadened lines superimposed on a continuous background. Unfortunately, the emission is a minimum in the region 2540-2600 Å, which is close to the threshold of rhenium. An image of the source is focused on the entrance slit of the monochromator by a 6-inch-diameter, off-axis parabolic mirror.

A small plate of glass, front-surfaced with aluminum, deflected a small portion of the light leaving the exit slit on to the sensitive surface of a 1P28 photomultiplier tube. This portion was used to measure the relative intensity of the light from the monochromator. The signal from the tube was displayed on a General Electric recorder. The remainder of the beam from the monochromator fell on the quartz lens of the experimental tube and was focused on the rhenium cathode.

A potential difference of 22-1/2 volts was used between the cathode and anode to collect the photo electrons. The rhenium cathode was isolated

from ground by a 3×10^{11} ohm resistor which acted as the load resistor for a FP54 electrometer tube. The electrometer system has a sensitivity of 182 cm/volt. With the chosen load resistor the galvanometer gave 1 cm deflection for a current of 1.8×10^{-14} amps. A voltage divider network, which gave incremental steps of approximately 15 millivolts, was used to calibrate the electrometer system.

The response of the photomultiplier system was found to be nonlinear with respect to changes in intensity. The system was calibrated by mounting the tube at various distances from a pinpoint light source and using the inverse square law to calculate the relative intensity of the light falling on a small hole in the light shield of the photomultiplier tube.

Several corrections had to be made to the galvanometer reading and photomultiplier reading before the correct value of photo current per unit incident light intensity as a function of the wavelength could be obtained. These corrections will be taken up in turn.

The first correction was that for the variation of the response of the photomultiplier tube with wavelength. This was given for the 1P28 by the S-5 spectral response curve in the RCA tube manual. The relative energy of a narrow wavelength band of light leaving the monochromator is found by dividing the photomultiplier intensity reading, I_p, by the relative spectral response for that wavelength $\alpha(\lambda)$, or $I_o = \frac{I_p}{\alpha(\lambda)}$ Actually, a correction should also be made for the variation of the reflection coefficient of aluminum with wavelength, but this effect is small over the wavelength's interval of interest and has been disregarded in this work.

A second correction was for the absorption of energy by the quartz lens of the experimental phototube. This is also a function of the wavelength of the light. To obtain a correction curve which was proportional to the absorption in the lens, the photomultiplier was used to plot two curves. One was of the energy distribution of the light from the monochromator when the light on the entrance slit passed through a quartz lens which was a mate of the one in the experimental tube; the other was an energy distribution without the lens. When the first of these curves is divided point by point by the second, a curve is obtained which is proportional to the absorption in the quartz. Thus, if $\beta(\lambda)$ is the absorption coefficient of the quartz lens and $\gamma(\lambda)$ is the curve obtained above, then $\gamma(\lambda) = C_1 \beta(\lambda)$ or $\beta(\lambda) = \frac{1}{C_1} \gamma(\lambda) = C_2 \gamma(\lambda)$. The energy of the light will be proportional to $\beta(\lambda) I_o(\lambda) = C_2 \gamma(\lambda) \frac{I_p}{\alpha(\lambda)}$

Fowler[13] and DuBridge[14] have developed graphical methods for analyzing photoelectric data. In the Fowler plot, the log of the photocurrent per unit relative light intensity divided by the square of the absolute temperature is plotted against $\frac{h\nu}{KT}$ This curve is then fitted by the well-known theoretical Fowler curve and the magnitude of the horizontal shift of the origin of the Fowler curve gives $\frac{h\nu_0}{KT}$, where ν_0 is the value of the threshold. The value of the vertical shift depends on the units and is not important here. Since the log of a proportionality constant simply shifts the curve vertically by a constant amount, one sees that proportionality constants may be disregarded and, for constant temperature to obtain the Fowler plot, one may plot $\log_{10}\left(\frac{L}{I_p}\frac{\alpha(\lambda)}{\gamma(\lambda)}\right)$ as a function of $\frac{h\nu}{KT} = \frac{hc}{\gamma KT}$ where L is the deflection of the galvanometer which measures the photocurrent.

A total of fifteen runs was made during the course of the experiment. For various reasons, only the values of Runs 11-15 were used to obtain the final value (these reasons included a noisy electrometer circuit which was finally cured by addition of a Sorensen regulator to the system and the discovery that the recorder was in error. It was replaced by a vacuum tube voltmeter). The values for the Runs 11-15 are listed below:

Run	λ_o	ϕ_o
11	2663 ± 7 Å	4.66 ± 0.02 ev
12	2653 ± 4 Å	4.67 ± 0.01 ev
13	2656 ± 4 Å	4.67 ± 0.01 ev
14	2665 ± 4 Å	4.65 ± 0.01 ev
15	2662 ± 7 Å	4.66 ± 0.02 ev

The average of Runs 11-15 is $\phi_o = 4.66 \pm 0.01$ ev.

In arriving at the above values of the limits, the following was considered:

(1) A mistake of 1 F in temperature will give approximately 1 Å error in λ_o.

(2) An error in the zero position of Fowler's curve of 0.2 gives approximately 3 Å error in λ_o.

(3) A slit width of 0.25 mm allows a bandwidth of approximately 5 Å at 2360 Å and approximately 7 Å at 2530 Å.

A correction was made for the fact that the monochromator reads about 3 Å too high in the region 2360-2530 Å.

In all of the experimental curves, the measured photocurrent at both the long wavelength and short wavelength ends of the region of interest seems to be less than what would be expected from the Fowler theory. It is fairly certain that this deviation is real, but because of the number of corrections that must be made to the data before they are in usable form, it cannot be said positively that the experimental apparatus is not introducing an error in the readings. Other investigators[15], however, have pointed out similar deviations from the Fowler curve.

The thermionic work function, 4.80 ev.[1], may be compared to the photoelectric work function, 4.66 ev. It has not been finally agreed whether the thermionic and photoelectric work functions for a pure metal should have the same value, but it is generally conceded they should be close. The thermionic and photoelectric work functions determined here do not agree as closely as those for tungsten, for which the thermionic work function is about 4.52 ev and the photoelectric work function about 4.50 ev.

MISCELLANEOUS PROPERTIES

Stability to the Water Cycle Reaction

Loss of metal from rhenium filaments by the water cycle mechanism was measured at various pressures of water vapor and compared with the rate of material loss from tungsten filaments under identical conditions. A summary of these measurements to June, 1954, was presented in WADC TR 54-371. One additional measurement of the water-cycle loss was made following that date, in which the best known vacuum techniques were employed to remove as much water vapor as possible. As in prior experiments, identically shaped tungsten and rhenium filaments were mounted in a U-tube, with a molybdenum collector cylinder around each filament. The gain in weight of each cylinder was the measure of the loss of metals from the filament. Each filament was operated at a brightness temperature of 1600 C for 222 hours. The gain in weight of the cylinder around the rhenium filament was 211 micrograms. This was 1.59 times the gain in weight of the cylinder around the tungsten filament.

At very low water vapor pressures, as in this experiment, the loss from each metal substantially due to evaporation only and the loss from water cycle reactions is negligible. The greater vapor pressure of rheni... is apparent from these measurements.

Stability to Attack by Aluminum Oxide

If used as a filament in electron tubes or as furnace heaters, one of the requirements of rhenium would be stability in contact with alumina. Based on a single test, this requirement is met by rhenium.

This test was conducted by wrapping a rhenium filament around a high-purity alumina sleeve and heating the filament in an evacuated chamber at a brightness temperature of 1600 C for approximately 7,000 hours. For comparison purposes, a tungsten filament in contact with alumina was inserted in the same chamber. It was heated at the same temperature and for the same length of time. The glass chamber was evacuated and baked for several hours before it was sealed off. The filaments were outgassed for two hours at a brightness temperature of 1800 C while the chamber was still being pumped. At seal-off, the indicated pressure was of the order of 10^{-7} mm of Hg. No getters were used.

There was no apparent reaction between alumina and either metal. See Figure 25. There was some darkening of the alumina sleeve in both cases, but it was more severe on the alumina around which the tungsten wire was wrapped. There was considerably more pitting of the tungsten filament, which was probably a result of another effect which was quite obvious in this test, viz., the much greater resistance of rhenium to the water-cycle effect. This was found in earlier work on this project[1]. The greater deposit of metal on the glass around the tungsten filament is apparent in Figure 26.

The Stability of Rhenium, Tungsten, and Molybdenum in Contact With Carbon-Bearing Atmospheres

In some applications, it is important that electron tube construction metals be in carbon-bearing atmospheres while at high temperatures. To evaluate the relative resistance of rhenium to these atmospheres, the carbonizability of rhenium, tungsten, and molybdenum were compared.

Wires of the three metals were heated electrically to 2325 C in a single chamber. A mixture of hydrogen and toluene vapor constituted the chamber atmosphere. The molybdenum wire carbonized and melted prior to one minute at 2325 C. After one minute the tungsten carbonized to about 20 per cent of its diameter. The wire was extremely brittle after carbonization. On the other hand, microscopic examination of the rhenium wire revealed no evidence of carbonization or a carbide or carbon-rich case. Further, there was no apparent change in the ductility of the rhenium as

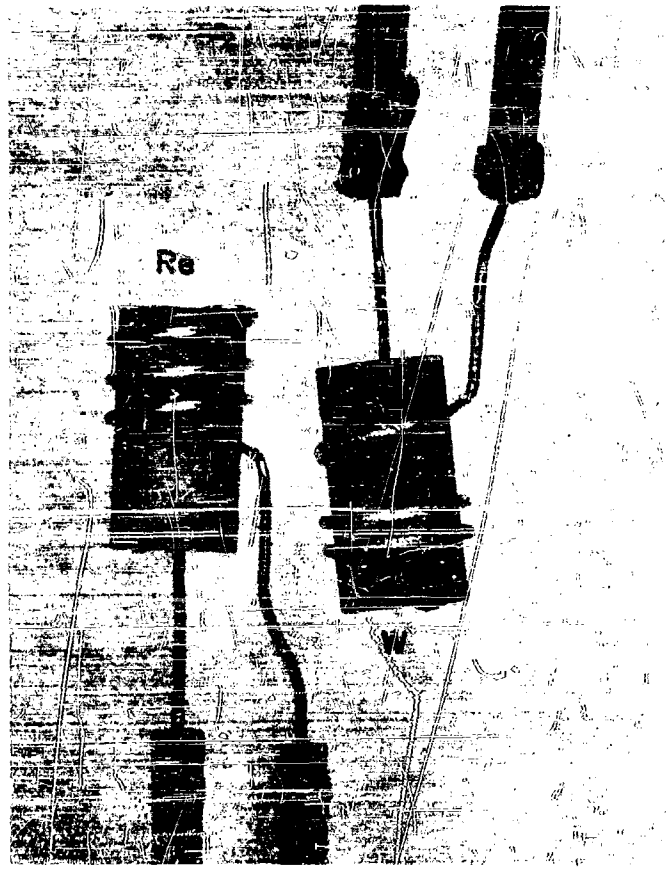

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FIGURE 25. THE APPEARANCE OF RHENIUM AND TUNGSTEN AFTER CONTACT WITH ALUMINA FOR 7000 HOURS AT A BRIGHTNESS TEMPERATURE OF 1600 C

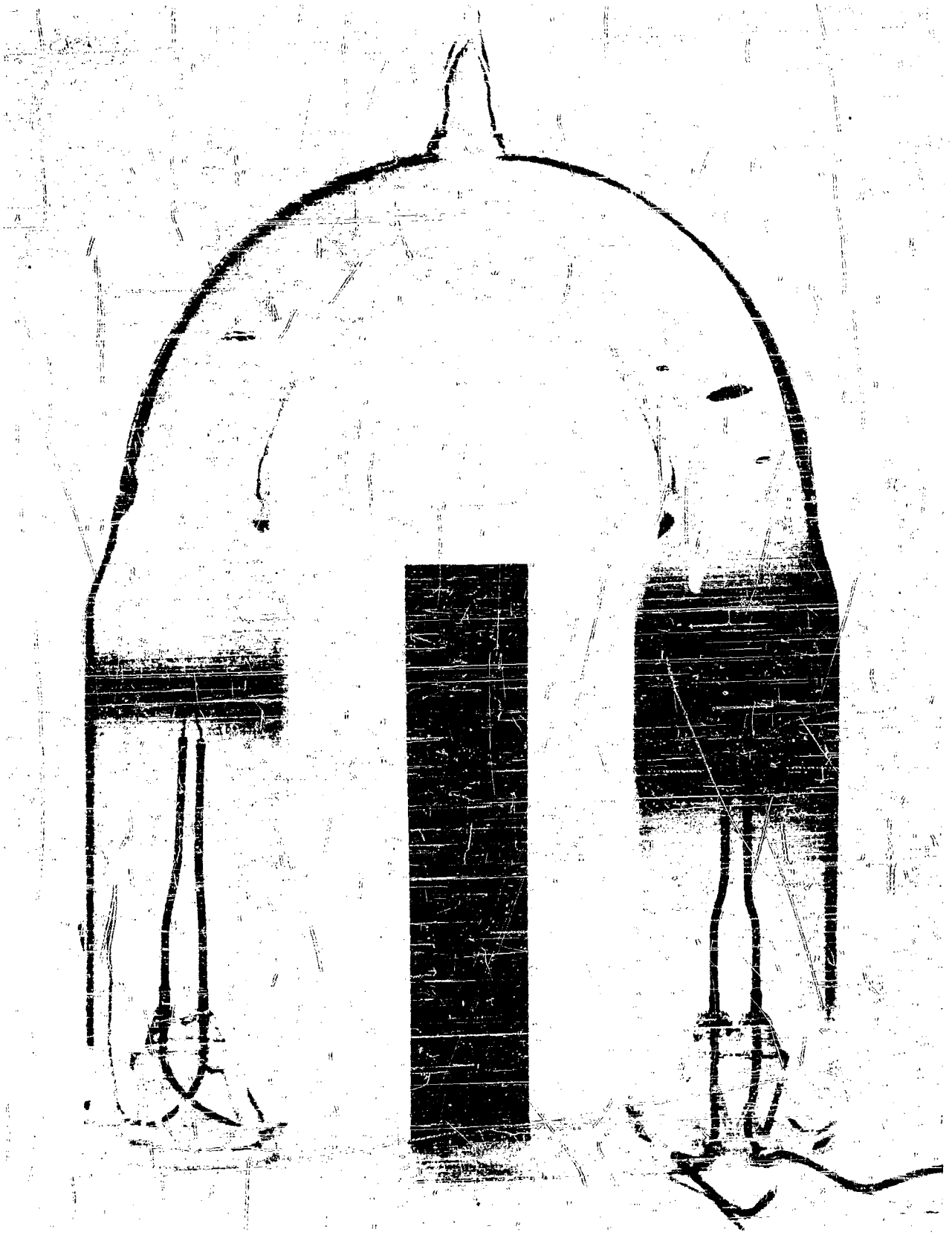

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FIGURE 26. THE CHAMBER FOR TESTING THE RESISTANCE OF RHENIUM TO ATTACK BY Al_2O_3

The greater resistance of rhenium to water cycling is apparent.

judged by hand bending; the hardness values were comparable to those of annealed rhenium wire. These results indicate that in applications where carbonization of the metal is undesirable, rhenium would be of great value.

Stability to Solution by Molten Metals

Previous studies in the current work indicated that rhenium might have very high resistance to molten metals. Recent work[1] on the evaporation of nickel by rhenium filaments further strengthened this view. To provide quantitative data, several studies of the resistance of rhenium to molten metals under static conditions were undertaken.

Two series of tests were conducted. In the first, short lengths of 60-mil rhenium wire were shaped into cones and suspended in molten metal 100 C above the melting point of the latter. Hydrogen atmosphere was used when the exposure temperature was above 650 C. Results reported in Table 7 show that rhenium is quite resistant to molten tin, zinc, silver, and copper, but is attacked slowly by aluminum and catastrophically by nickel and iron under these conditions. To establish whether the poor resistance of rhenium to molten iron and nickel may have been due to the excess of solvent metal present, a second series of tests was devised. In these studies, a small hollow was indented into a 1/2- by 1-inch rectangle of 5-mil rhenium foil. About 1 gram of iron was placed in the hollow, and the test panel exposed for 1 hour at 1640 C. The same procedure was followed for nickel as for iron, but at a temperature of 1550 C. In both cases, the molten solvent metal dissolved nearly all of the 5-mil rhenium sheet in contact with it. In this case, the total available weights of solvent and solute metal were approximately equal.

TABLE 7. ATTACK OF RHENIUM[a] BY MOLTEN METALS

Solvent Metal	Exposure Time, hours	Temperature, C	Decrease in Diameter, inch	Weight Loss, gram
Tin	1.0	330	0.0001	0.0032
Zinc	1.0	520	0.0001	0.0160
Aluminum	1.5	760	0.0097	0.4239
Silver	1.0	1060	0.0000	0.0051
Copper	1.0	1180	0.0000	0.0021
Nickel	2.0	1550	Specimen entirely dissolved	
Iron	1.0	1650	Specimen entirely dissolved	

(a) 60-mil wire immersed about 1/2-inch.

These data show that rhenium has little resistance to attack by molten iron or nickel, but remains undamaged by lower-melting metals such as tin, zinc, copper, and silver. Aluminum reacts slightly with rhenium. Thus, rhenium, which occasionally has been suggested as a possible material for direct-immersion thermocouples in iron or its alloys, apparently is not sufficiently inert to molten iron. It would, however, be quite useful in contact with the other metals investigated. This information is partially in conflict with findings at Westinghouse (see p. 75) where rhenium has been used successfully to evaporate molten nickel.

STABILITY OF RHENIUM AND TUNGSTEN SUBJECTED TO MECHANICAL AND THERMAL SHOCK

Rhenium and tungsten differ in that rhenium is ductile following heating above its recrystallization temperature, while tungsten becomes brittle. This indicates that a rhenium filament might have superior resistance to mechanical shock or shaking after having been heated; if so, it might become an important material of construction for "ruggedized" electron tubes. To study this effect, rhenium and tungsten wires were thermally cycled to recrystallization temperatures while simultaneously being mechanically shaken.

Two tubes were constructed for the shake test, each containing a 5-mil-rhenium and a 5-mil-tungsten wire, as illustrated in Figure 27. The wires, approximately 2 inches in length, were attached to 1/8-inch-diameter nickel support rods by inserting the wires in slits and using a resistance welder to flow nickel around the wires. This method of attachment was employed to reduce premature recrystallization of the wires at the joints. The wires were outgassed at 1600 C while the tubes were attached to the pumping system, and the tubes were then sealed off. During testing, the wires were cycled from room temperature to 1200 C brightness temperature by resistance heating with a heating-duty cycle of 6 seconds on and 6 seconds off. Because of the small diameter of the wire, the temperature was difficult to read by an optical pyrometer, and the accuracy of the temperature measurement was probably poor.

Initially, the tubes were mounted directly on a shake table. However, it was found that the maximum acceleration obtained was only 4 g's, so the tubes were mounted at the ends of a bar, the center of which was attached to the tube. With this arrangement, maximum acceleration greater than 120 g's was obtained when the tubes were shaken at a frequency of 200 cps.

With the final arrangement, the tubes were shaken for 17 hours at 200 cps and 15-1/2 hours at 80 cps. Using the second arrangement, the

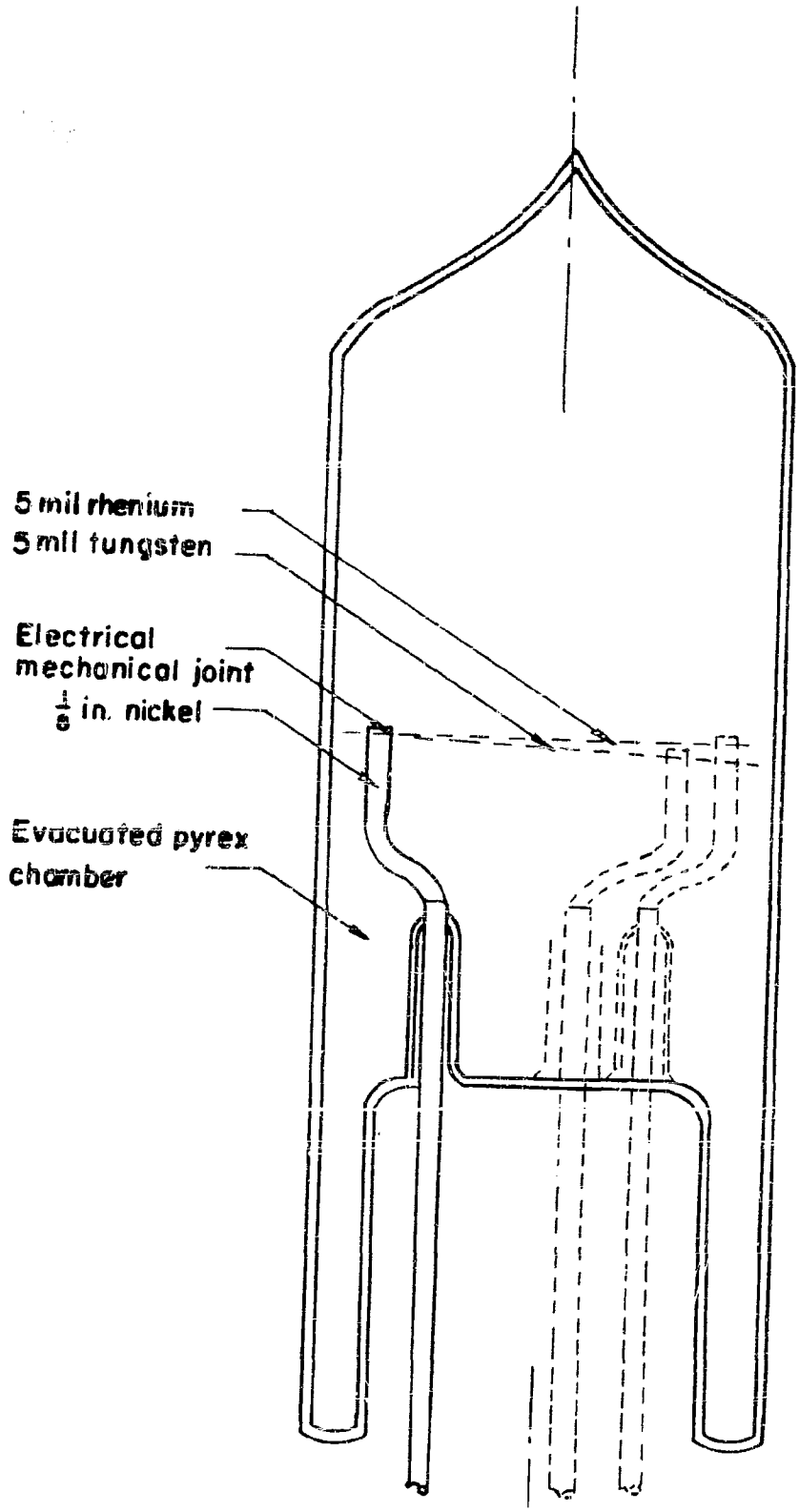

FIGURE 27. MOUNTING ARRANGEMENT OF RHENIUM AND TUNGSTEN WIRES FOR VIBRATION TESTS

Direction of motion was nearly perpendicular to length of wires.

same tubes were shaken for 32-1/2 hours at 200 cps. At the end of this time, there was no sign of any change in either the tungsten or the rhenium. This phase of the investigation was then discontinued as the rhenium investigation terminated. Further reliability testing of this sort would be necessary to obtain a separation in behavior between the rhenium and the tungsten. Also, temperature cycling to higher temperatures would be expected to produce more accelerated effects.

PROPERTIES OF PLATINUM-RHENIUM ALLOYS

A portion of the current research program was devoted to investigation of the effect of small additions of rhenium on the properties of platinum. Initial plans were to investigate alloys containing up to 10 weight per cent rhenium, but difficulties in fabrication prevented preparation of wire containing more than 2 per cent rhenium. The fabrication procedures used to prepare this wire and the physical and mechanical properties of these alloys are discussed below.

Fabrication of Platinum-Rhenium Alloys

Buttons weighing 10 grams and containing 2, 5, and 10 per cent by weight of rhenium in platinum were arc-melted. Fabrication attempts, including cold working with intermediate anneals and hot working both from hydrogen and air atmospheres, were all unsuccessful because of cracking after a few per cent reduction. In all cases, the 2 per cent rhenium alloy was found to be more fabricable than alloys containing more rhenium.

Attempts to fabricate the 10 per cent rhenium alloy were then abandoned and a virgin 1 per cent alloy was melted. When hot-working proved still unsuccessful, it was suspected that contamination by iron from the working surfaces was hardening the alloys. New alloys were melted from virgin stock, and in subsequent working attempts a hydrochloric acid pickle was included. After this remelting, the three alloys, 1, 2, and 5 per cent rhenium, were hot worked from 1000 C in air to approximately 1/4-inch square cross-sections by hand hammer forging. Anneals for 30 minutes at 1000 C were given after each 10 per cent total work. Following squaring of the buttons, they were hot rolled from 1000 C in diamond-shaped grooved rolls to 80-mil rods. The 5 per cent rhenium alloy cracked badly in the first pass and was abandoned. The 2 per cent rhenium alloy developed one slight crack which did not propagate. Reduction from one groove to the next was about 15 per cent, although two passes were made through each groove. Anneals for 30 minutes at 1000 C were given very

frequently at the start of rod rolling, but were decreased uniformly so that at the end of rolling, when the rods had reached the minimum dimension of about 80 mils, one anneal was being given only after about a 60 per cent reduction.

The 80-mil rods were hot swaged at 1000 C to 60-mils diameter, annealed, and cleaned. The swaged rods were then cold drawn to 45 mil wire, with anneals after each 20 to 30 per cent reduction. Wire tensile tests were conducted and 20-mil wire suitable for use as thermocouples was prepared by additional cold drawing.

Electrical Resistivity of Platinum-Rhenium Alloys

Twenty-mil wire of two alloys, Pt-1.0 Re and Pt-2.0 Re, and of pure platinum were measured to find the electrical resistivity at room temperature. Lengths of 27.75 cm were measured for electrical resistance in a Kelvin bridge at constant temperature. The values obtained, compared to the accepted value for pure platinum, are as follows:

Metal	Resistivity at 25 C, microhm centimeters
Pt-1.0 Re	19.9
Pt-2.0 Re	25.8
Platinum (this work)	11.0
Platinum (literature)[3]	10.94

The value for pure platinum is within about 0.05 per cent of the literature value, giving an indication of the accuracy of the measurements.

The increase of resistivity caused by rhenium is compared with that caused by rhodium and ruthenium alloy additions in Figure 28. Rhenium appears to increase the resistivity markedly and at a somewhat higher rate than either ruthenium or rhodium. Small additions of rhenium to platinum would be expected to greatly increase the heating efficiency of platinum in applications where the metal is used for resistance heating, as in furnace elements or elements in resistance thermometers.

Thermal Electromotive Forces Produced by Platinum vs Platinum-Rhenium Alloys

Thermocouples prepared from Pt-1.0 Re and Pt-2.0 Re alloys welded to pure platinum were placed in a protection tube in a molybdenum-wound

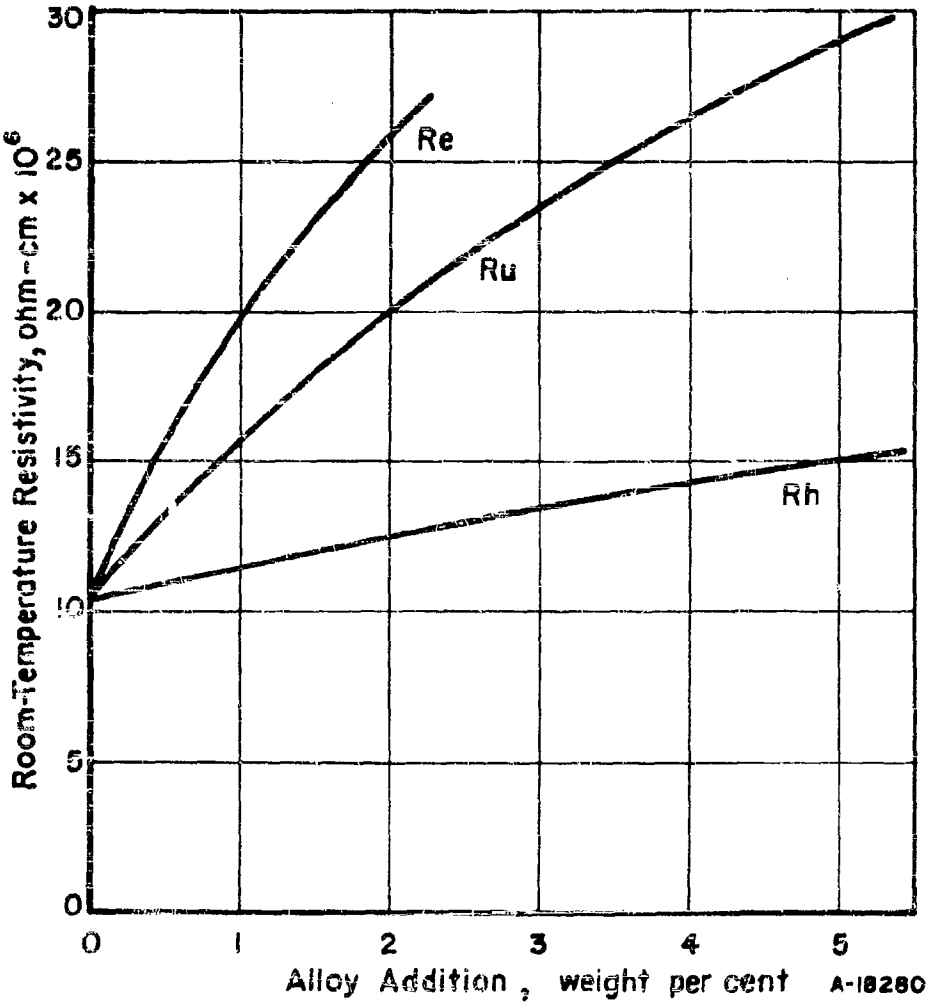

FIGURE 28. ELECTRICAL RESISTIVITY OF SEVERAL PLATINUM ALLOYS

tube furnace containing a reducing atmosphere. Two Pt-Pt10 Rh thermocouples were also included, so that the beads of all thermocouples were together in a hole in a temperature-equalizing body consisting of a small block of molybdenum. The thermal emf's generated are given in Figure 29, compared with previous data for 1200C as reported by Schulze[10].

Rhenium additions to platinum cause generation of a positive usable emf when the alloys are coupled to pure platinum. Pt-2.0 Re alloys generate a slightly higher emf than Pt-1.0 Re alloys for any given temperature. Early and limited data by Schulze generally agree with the findings of the present work, but indicate that a greater difference in potential might be expected between the Pt-1.0 Re and Pt-2.0 Re alloys against platinum. No chemical analysis was performed on the present platinum-rhenium alloy wires; actual composition may have been slightly different from the nominal 1.0 per cent difference in rhenium between the alloys.

Mechanical Properties of Platinum-Rhenium Alloys

Tensile Strength and Ductility

Annealed Pt-1.0 Re and Pt-2.0 Re alloy wires, 20 mils in diameter, were tensile tested to provide information on mechanical properties. The results are given in Table 8.

TABLE 8. MECHANICAL PROPERTIES OF PLATINUM AND PLATINUM-RHENIUM ALLOYS

Material	Hardness, VHN[a]	Ultimate Tensile Strength, psi	Elongation in 2 inches, per cent	Reduction of Area, per cent
Pt-1.0 Re	139	77,000	15	12
Pt-2.0 Re	151	78,100	12	7
Pt-5.0 Re	196	--	--	--
Platinum[6]	~40	20,000	35	--

(a) 5-kg load.

Rhenium additions to platinum increase its tensile strength nearly fourfold, as might be expected from the marked hardening effect of rhenium noted below. The ductility decreases correspondingly. One per cent rhenium added to platinum produces the greatest strengthening effect, while the two per cent rhenium shows very little increase in strength.

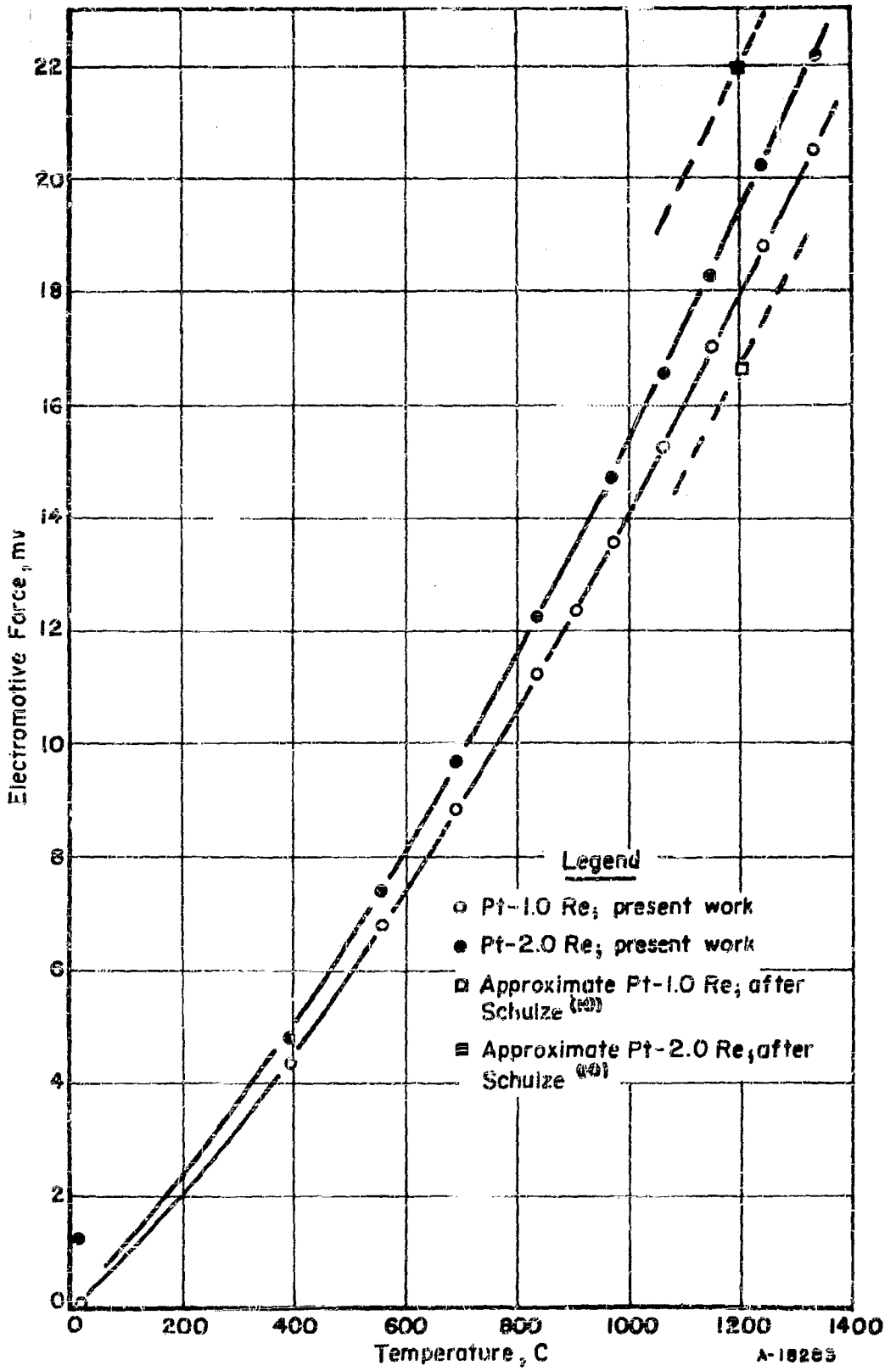

FIGURE 29. THERMAL ELECTROMOTIVE FORCE DATA FOR Pt-1.0Re AND Pt-2.0Re VERSUS PLATINUM

Hardness

To avoid cracking during fabrication of the Pt-1.0 Re, Pt-2.0 Re, and Pt-5.0 Re alloys, hardness measurements were taken for control purposes. About 12 anneals were given during hot hand-hammer forging. The VHN values taken after each anneal were averaged to give the hardnesses for alloys annealed, after working, at 1000 C for 1/2-hour (Table 8).

Figure 30 shows that the annealed hardnesses of the worked platinum-rhenium alloys were higher than the annealed hardnesses of the as-cast Pt-Re alloys reported previously[1]. This effect is expected, and is probably due to the finer grain size in the worked alloys. Figure 30 also shows data from Vines and Wise[3] on the hardening of platinum by rhodium and nickel. Since nickel hardens platinum more than any of the other nine hardening agents reported by Vines and Wise, the data of the present work support the conclusion that rhenium has the greatest hardening effect on platinum, on a weight basis. However, nickel is much less dense and expensive than rhenium, and would be a more economical hardening agent on the basis of cost per unit weight.

Oxidation Resistance of Platinum-Rhenium Alloys

Alloys of platinum-rhenium may be of interest for thermocouples or other applications where the alloy must exhibit good oxidation resistance. To establish whether rhenium affects the excellent oxidation resistance of pure platinum, the Pt-1.0 Re and Pt-2.0 Re alloys were exposed to air at elevated temperature in series of tests with pure platinum. Twenty-mil wires of each metal were coiled on mandrels to decrease the over-all specimen size, then exposed to uncontrolled air for 1, 10, and 100 hours at 800 C. The weight change is recorded in Table 9.

TABLE 9. OXIDATION OF PLATINUM AND PLATINUM-RHENIUM ALLOYS IN AIR AT 800 C

	Cumulative Weight Change, mg, After Indicated Exposure		
	1 Hour	10 Hours	100 Hours
Pt-1.0 Re	-0.8	+0.1	+0.4
Pt-2.0 Re	-0.5	-0.4	+0.5
Platinum	-1.0	-0.4	+0.2

Possibly due to removal of impurities from the surface or to removal of hydrogen in solution as a result of exposure of the specimens to a reducing atmosphere prior to the test, all specimens lost some weight in the first hour. After that, all specimens gained weight at a very slight rate up

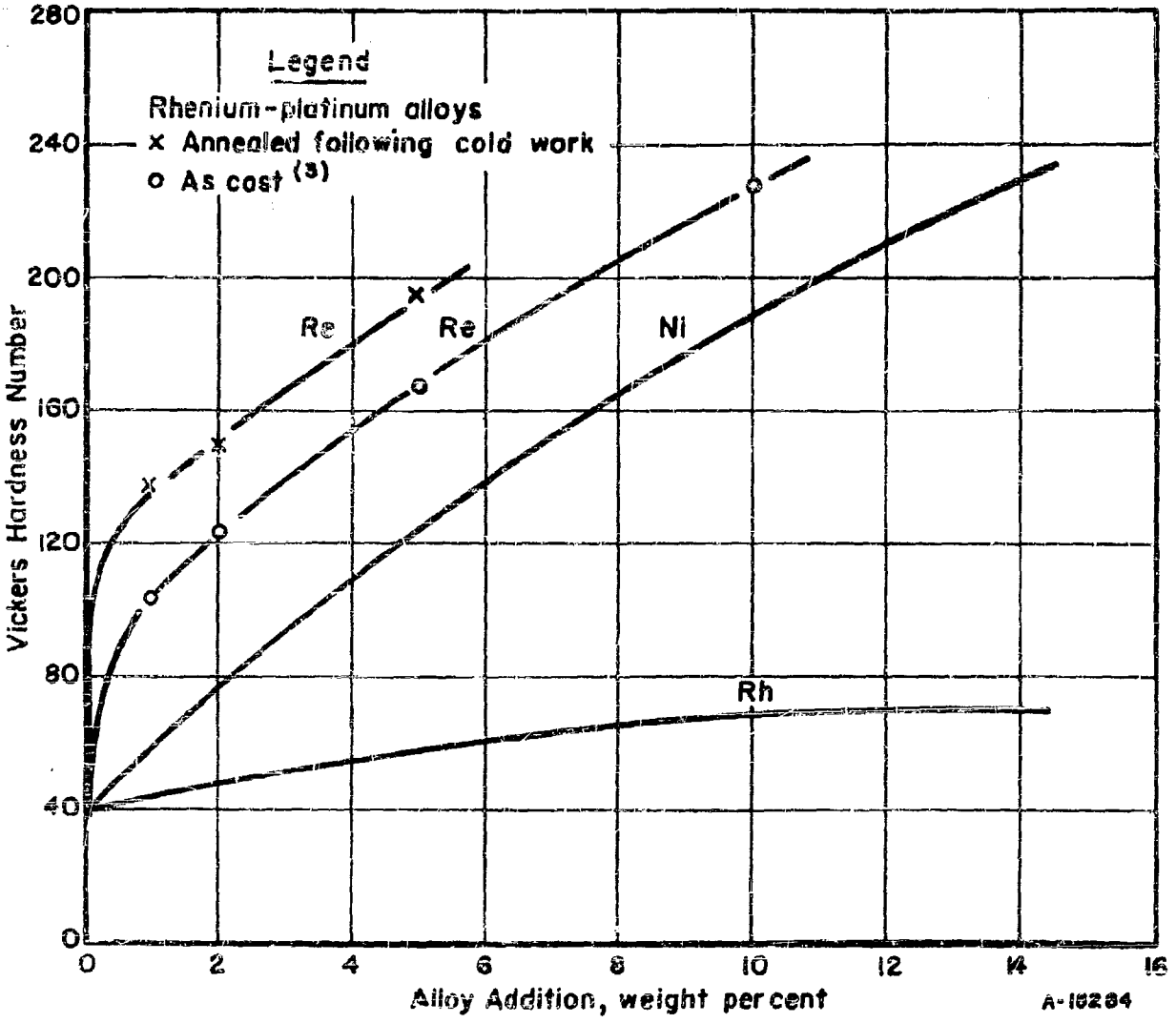

FIGURE 30. THE EFFECT OF RHENIUM AND OTHER METALS ON THE HARDNESS OF PLATINUM

to conclusion of the test at 100 hours. The results indicate that the rhenium alloys may be very slightly less resistant to air oxidation than pure platinum. To establish the difference between the Pt-Re alloys and platinum more positively, longer times and higher temperatures would be required.

DISTRIBUTION OF INFORMATION AND MATERIALS

The distribution of information about rhenium and rhenium specimens for experimental purposes has continued at a high level in order to acquaint educational and industrial organizations with the metal. Experimental quantities of rhenium metal in the form of powder, sheet, rod, or wire were given to those interested organizations that agreed to transmit their over-all experimental results in return. The latter service was terminated in February, 1955, so that the recipients of rhenium stock would have ample time to complete their experiments and transmit results to us. Rhenium samples were sent to 20 organizations on the list published in WADC TR 54-371 and in the list below. Recently, an inquiry was mailed to all who had received rhenium, but who had not contacted us concerning their results. Of the group of 20 given metal, 12 had worthwhile information to report, the recent portion of which is reviewed below. Several more organizations recently responded that work has not yet commenced on their rhenium specimens. Four or five organizations have not answered.

Organizations Contacted

The industrial organizations listed below are those who have been contacted in connection with rhenium information or samples. The list does not include contacts made for requests of reprints only, and is in addition to that in TR 54-371, which contained 40 names.

1. Aluminum Company of America
2. Associated Electrical Industries, Limited
3. A. W. Haydon Company
4. Baker and Company, Inc.
5. Bell and Howell Company
6. Bendix Aviation Corporation, Red Bank Division
7. British Joint Services Mission (Navy Staff)
8. Braunschweig University
9. California Institute of Technology
10. Carlton-Cook Plating Corporation
11. Central Sales and Manufacturing Company
12. City Chemical Corporation

13. Campagnie Francaise Thomson-Houston
14. Convair, General Dynamics Corporation
15. Decker Aviation Corporation
16. Department of Commerce
17. Department of The Air Force
    - Aeronautical Research Laboratory
    - Air Force Cambridge Research Laboratory (Battelle Research Project)
18. Department of The Interior
19. Eastern Products Company
20. Electric Autolite Company
21. F. J. Stokes Machine Company
22. Food Machinery and Chemical Corporation
    - Becco Chemical Division
23. Franklin Institute
24. General Electric Company
    - Aircraft Nuclear Propulsion Division
    - General Purpose Control Department
    - Large Lamp Department
    - Locomotive and Car Equipment Department
    - Trumbull Components Department
    - Tube Department
    - X-Ray Department
25. H. A. Wilson Company
26. Institute for the Study of Metals
27. Kearfott Company
28. Kemet Company
29. Lewis and Kaufman, Ltd.
30. Line Material Company
31. L. Light & Co., Ltd.
32. Machlett Laboratories
33. Massachusetts Institute of Technology – Project Lincoln
34. Metals and Controls Corporation
35. Mine Safety Appliances Company
36. Molybdenum Corporation of America
37. Museum of Science and Industry
38. Oak Ridge National Laboratory
39. Parker Pen Company
40. Philips Laboratories, Incorporated
41. Phillips Petroleum Company
42. Radio Corporation of America
43. Sperry Gyroscope Company
44. Standard Register Company, The
45. Times Facsimile Company
46. Titanium-Zirconium Company, Incorporated
47. Welsbach Corporation, The

48. Westinghouse Electric Company
    Lamp Division
    Electronic Tube Division
49. University of Michigan

Research Reported by Various Educational and Industrial Organizations

Information received from organizations who conducted experimental research on rhenium metal supplied by this project is reported below by subject. A group of three reports of this type is included in WADC TR 54-371.

Wear Resistance

Rhenium was evaluated for wear resistance as a phonograph needle by Permo, Inc., of Chicago, Illinois. Rhenium had good wear resistance, but was not as good as commercial alloys currently in use.

Field Emission

Work at Linfield College, McMinnville, Oregon, showed that rhenium is an excellent filament for field emission use. One advantage of rhenium is that it apparently develops a clean surface more readily than tungsten, so that a clearer pattern results.

Work of this type, and in agreement with the Linfield College findings, was done at the Research Laboratory of the General Electric Company, Schenectady, New York. In the latter work the etched emitting tip enlarged at elevated temperatures, so the work was terminated. Studies of this property at the California Institute of Technology were not followed through to tangible results.

Electron Ejection Target

Rhenium ribbon has been rolled and fabricated to target shape for use in a study of electron ejection by ion bombardment at Bell Telephone Laboratories, Murray Hill, New Jersey. Experimentation with the finished apparatus has not commenced.

Vacuum Lamps

At the Lamp Division of the General Electric Co., Nela Park, Cleveland, Ohio, rhenium filaments were compared with tungsten filaments in vacuum lamps. The lumens per watt light emission was essentially the same for both materials. The rhenium showed superior "water cycle" resistance and the tungsten showed better "life test" results.

X-Ray Micro-Focus Tube

Efforts to install rhenium in a micro-focus tube at John Hopkins University, Baltimore, Maryland, were unsuccessful when attempts to draw the wire from 20 to 6 mils failed.

TR Switching Tubes

An electronics concern evaluated rhenium as ignitor electrodes in transmitting-receiving switching tubes. In general, rhenium was successful in the application, although the tubes failed due to other causes.

Glass-to-Metal Seals and Machinability

The Raytheon Manufacturing Company, Waltham, Massachusetts, successfully sealed rhenium metal wire to a ceramic washer. The seal was vacuum tight. A seal of 1/4-inch rhenium rod to ceramic was not so successful, apparently due to a crack in the rod. Raytheon also successfully cut rhenium with a high-Al_2O_3 ceramic tool bit.

Corrosion Resistance

The Raytheon Company also found rhenium had good resistance to salt spray corrosion.

Gauge Tube

The life of rhenium was compared to tungsten in a VGIA standard gauge tube by the Central Sales & Manufacturing Corporation of Denville, New Jersey. Under equivalent conditions, the rhenium burned out between 1000 and 1100 hours, while the tungsten was still in good operating condition at about 1275 hours. The burn-out was attributed to normal evaporation.

Stylus Material

Rhenium has equivalent life to tungsten when evaluated as a cutting stylus on facsimile equipment by the Times Facsimile Corporation. Since tungsten costs less, its position is more favorable.

Evaporation Filament

The Westinghouse Electric Corporation, Churchill, Pennsylvania, has reported that rhenium is very successful when used to heat silver and nickel for vapor coatings of the latter metals. It has a considerably longer life than tungsten. Rhenium wire will also be tested in a Bayer-Alpert vacuum gage.

Spectral Emissivity

Marple[16] determined the spectral emissivity of rhenium at 0.65μ at the General Electric Company. These results were reported in detail in the literature-survey appendix of the Thirteenth Quarterly Progress Report, January 15, 1956.

SUMMARY

Rhenium metal powder of high purity was prepared through a chloride-hydrolysis process. In this method, rhenium metal was chlorinated to $ReCl_5$, which was subsequently hydrolyzed to finely divided ReO_2. The ReO_2 was reduced to the high-purity metal powder.

Fabrication studies were conducted on the halide-process rhenium. The metal powder pressed to 56 per cent of theoretical density, the highest as-pressed density recorded in this work. However, sintering at 2700 C only produced further densification to 79 per cent of theoretical. Perrhenate-type rhenium normally sinters to 90-95 per cent of theoretical density. The halide-process bar was successfully rolled to 30-mil sheet.

Alloys containing 2, 5, and 10 per cent rhenium in platinum could not be fabricated initially by the common methods of hot or cold working. However, alloys containing 1, 2, and 5 per cent rhenium were finally successfully hot worked to square ingots at 1000 C in air when careful procedures to eliminate contamination by iron were introduced. The alloys containing 1 and 2 per cent rhenium were worked to wire by shape rolling and wire drawing.

The electrical resistivity of rhenium at room temperature (20 C) was redetermined as 19.3 ohm-cm x 10^{-6}. The elevated-temperature resistivity was also rechecked by four series of resistivity measurements, each series being over a different temperature range from room temperature to 2425 C. All of this data was combined with the data obtained at room temperature to give a curve relating temperature and electrical resistivity over the entire temperature range. The resistivity increases from 19.3 microhm-centimeters at room temperature to about 110 microhm-centimeters at 2425 C. It follows the expression:

$$\rho' = -4.5 + 90.0 \times 10^{-3}T - 23.5 \times 10^{-6}T^2 + 2.2 \times 10^{-4}T^3 ,$$

where ρ' is the resistivity in microhm-centimeters and T the temperature in degrees Kelvin. Two per cent rhenium in platinum increases the electrical resistivity to 25.8 microhm-centimeters compared to 10.94 for pure platinum.

The specific heat of rhenium was determined from 1620 to 2690 K, by a method in which the heat input to a rhenium wire was increased in a step. An oscilloscope was used to measure traces of the time-temperature relationship and the specific heat calculated. A plot is included in the text showing the specific heat to be higher than that of tungsten at elevated temperatures. Accuracy of the vapor pressure measurements reported in the previous technical report was questioned, so a discussion is included in the text.

The electromotive force produced by the platinum-rhenium thermocouple follows the following power series equation:

$$E = 1.56 - 0.90 \times 10^{-2}T + 1.29 \times 10^{-5}T^2 ,$$

where E is the voltage in millivolts and T is the temperature, K. The first derivative of this equation gives the thermoelectric power, P, in microvolts per degree as a straight-line function:

$$P = -9.0 + 2.58 \times 10^{-2}T .$$

Thermoelectric potential studies were next completed on rhenium vs tungsten, molybdenum, and tantalum, and on rhenium-platinum alloys vs platinum. Rhenium produces essentially linear thermoelectric-force variations with temperature with tungsten or molybdenum above 1700 C. At 2500 C, the Re-W couple gave 28 mv and the Re-Mo couple gave 21 mv. The Re-Ta couple produces an erratic emf from room temperature to 2500 C. Rhenium-platinum alloys containing 1 and 2 per cent rhenium were measured for thermoelectric effect against pure platinum. At about 1350 C, the Pt vs 1.0 Re-Pt and Pt vs 2.0 Re-Pt couples produce emf's of about 21.0 and 22.5 mv, respectively.

Ten-mil rhenium sheet was cold rolled up to 30 per cent reduction, and the tensile properties determined for the as-worked and as-annealed conditions. The strength and ductility of annealed sheet is similar to that of annealed swaged rod. The cold-rolled sheet has an ultimate tensile strength of 322,000 psi, but rather low ductility. Studies were also completed on the work-hardening characteristics of rhenium wire and sheet. Results show that 60-mil wire, and 10- and 150-mil sheet all work harden at a slower rate and to a lesser degree than swaged 150-mil rod, for which data have been reported previously. With 40 per cent reduction in cross-sectional area, the 150-mil sheet work hardens to about 700 VHN and the wire to 600 VHN. The thin 10-mil sheet, however, work hardens to only about 450 VHN. Apparently rounds work-harden more seriously than flats, and thick sections more than thin sections.

The temperature-dependency of the modulus of elasticity was studied and found to decrease approximately linearly up to 880 C. The shear modulus at room temperature was also studied, and found to be 22.6×10^6 psi. A calculation of Poisson's ratio from this and the Young's modulus data previously reported gives a value of 0.49. The stress-rupture behavior of rhenium was investigated and related to the elevated-temperature short-time tensile data by a Larsen-Miller plot. At 2000 C, the maximum temperature for which data were obtained, rhenium has a rupture time of 12.3 hours at 1100 psi. The ductility drops off markedly at 500 C, to about 1 or 2 per cent elongation, then at 2000 C, ductility increases again.

It was found that rhenium hardens platinum more than other known additive elements, and that 1 or 2 per cent rhenium increases the tensile strength of annealed platinum to about 78,000 psi and lowers the elongation to about 12 per cent. These alloys have about the same oxidation characteristics in air as pure platinum.

A study of the thermionic emission of rhenium containing 2.0 per cent thorium (as ThO_2), gave a work function of 2.7 ev with a corresponding A value of 0.01 amp/cm^2. Thus neither 0.5, 1.0, or 2.0 per cent thorium produce as much enhancement of emission as corresponding amounts of ThO_2 do in tungsten. The photoelectric work function of rhenium was measured by determination of the photoelectric threshold using Fowler's method. The work function, ϕ_o, is 4.66 ± 0.01 ev or a threshold wavelength, λ_o, of 2662 $\pm$ 4 Å. The thermionic work function of rhenium was found earlier to be 4.80 ev.

A further determination was completed in connection with the water-cycle effect. A tube containing both tungsten and rhenium was evacuated to allow the presence of very little water vapor. The weight loss from rhenium was 1.59 times that from tungsten, since the water-cycle effect became negligible and vapor-pressure losses predominated. Rhenium is quite resistant to attack by molten tin, zinc, silver, and copper; although attacked slowly by aluminum and very rapidly by nickel and iron. Rhenium was

exposed to solid Al_2O_3 at 1600 C in a life test with a tungsten filament, exposed under identical conditions for comparison purposes. Neither filament had failed after 7000 hours of operation, although at completion of the test the tungsten was found to be seriously pitted by water-cycle attack. Rhenium, tungsten, and molybdenum filaments were also exposed to a carbonaceous atmosphere at 2300 C for one minute. The tungsten carburized and became brittle, and the molybdenum burned out. However, the rhenium apparently retained its original ductility and was virtually unaffected. This tends to support information that rhenium does not form a carbide.

The text of the report includes summaries of rhenium investigations conducted at some of the educational and industrial organizations to which samples of rhenium metal prepared in this work had been given.

Rhenium and tungsten filaments were thermally cycled to 1200 C from room temperature while being mechanically shaken. After 32-1/2 hours at over 120 g's (200 cps) plus earlier less severe shaking, neither filament had shown signs of failure.

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